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REACTOR FUEL PROCESSING

A Quarterly Technical Progress Review

Prepared for DIVISION OF TECHNICAL INFORMATION, USAEC, by
STEPHEN LAWROSKI and ASSOCIATES, ARGONNE NATIONAL LABORATORY

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TECHNICAL PROGRESS REVIEWS

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REACTOR FUEL PROCESSING

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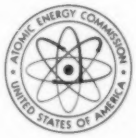

Foreword

This quarterly review of reactor fuel processing has been prepared at the request of the U. S. Atomic Energy Commission, Division of Technical Information. It is intended to assist those interested in keeping abreast of important developments in this field. In each Review it is planned to cover those particular subjects in which significant new results have been obtained. The Review does not purport to abstract all the literature published on this field during the quarter. Instead it is intended to bring each subject up to date from time to time as circumstances warrant.

Interpretation of results, where given, represents the opinion of the editors of the Review, who are personnel of the Argonne National Laboratory, Chemical Engineering and Idaho Divisions. Those taking part in the preparation of this issue are J. Barghusen, L. Burris, Jr., P. Fineman, A. A. Jonke, S. Lawroski, W. J. Mecham, D. Paige, J. Royal, J. Simmons, R. K. Steunenberg, C. E. Stevenson, and R. C. Vogel. The reader is urged to consult the original references for more complete information on the subject reported and for the interpretation of results by the original authors.

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Section

I

Reactor Fuel Processing

Commercial Aspects of Fuel Processing

Fuel-Processing Plans

An increasing number of nuclear-fuel-processing plants are either in operation or in some stage of design or construction in various countries of the world. In order to assist the readers of *Reactor Fuel Processing* in keeping straight the locations and some of the important characteristics of these plants, the list shown in Table I-1 has been prepared. Only plants capable of processing irradiated fuels are listed; plants for recovering unirradiated scrap are not included. Pilot plants that are primarily for process development, such as the Oak Ridge facilities, are not included; however, the Italian pilot plant for irradiated thorium fuels is listed since it will process cores from operating reactors.

Of the plants listed, the Nuclear Fuel Services, Inc. (NFS), plant in the United States and the EUREX plant in Italy are in very early stages of construction, and, presumably, plans for construction of these plants could still be changed. The Japanese plant, for which design is just getting under way, will probably not be needed until 1968 to 1970, based on the expected installation of nuclear power facilities in that country.[1]

In addition to the plants listed in Table I-1, announcements have been made of studies which could lead to other future processing plants. Australia is giving serious consideration to the possibility of building a small plant primarily to serve its own processing needs. This decision resulted largely from the difficulties and expense of arranging for shipment of spent fuel from Australia's test reactor to Britain for processing. One of the processes that Australia is known to be considering is a fluidized-bed fluoride-volatility process (see Sec. III).[2]

Reports from Germany indicate that serious consideration is being given to the possibility of building a pilot processing plant to serve German reactors and to provide German industry with experience in this field. The plant would have a capacity of 30 tons of low-enriched fuel per year.[1]

In the United States the General Electric Company and Allied Chemical Corp. have announced that they have undertaken a joint engineering study to develop a nuclear-fuel-recovery process for power-reactor fuels and that the study will be completed during 1963 in sufficient detail to determine the capital, operating, and maintenance costs of the plant. The process under consideration is said to involve fluoride-volatility processing, and the plant size under study is believed to be considerably smaller than the planned NFS plant. The announced goals of the study are "to attain major advances in ... relative plant size for economic fuel recovery, integrity of radioactive waste containment, and siting acceptability for the fuel-recovery facility."[1]

Transportation of Irradiated Fuel

In December 1962 the AEC Divisions of Licensing and Regulation, Operational Safety, and Reactor Development sponsored a symposium in Germantown, Md., on "Packaging and Regulatory Standards for Shipping Radioactive Material." A report consisting of a compilation of papers presented and comments made by participants at the symposium has been issued.[3] The symposium dealt largely with the development of regulatory standards for shipping-cask design and the methods and problems involved in designing, evaluating, and approving casks.

Table I-1 EXISTING AND PROPOSED PROCESSING PLANTS FOR IRRADIATED NUCLEAR FUELS

Plant	Country	Approximate capacity	Fuel type	Status	Plant ownership
Idaho CPP	U. S.		High enrichment	Operating	USAEC
Savannah River	U. S.		High and low enrichment	Operating	USAEC
Hanford	U. S.		Low enrichment	Operating	USAEC
Nuclear Fuel Services, Inc.	U. S.	1 ton/day*	High and low enrichment	Completion expected in 1965	Private corporation
Dounreay	Britain	3000 kg/year	High enrichment	Operating	UKAEA
Windscale	Britain		Low enrichment	Completion expected in 1963	UKAEA
Eurochemic	Belgium	50 tons/year	Low enrichment	Completion expected in 1964	European Nuclear Energy Agency
Marcoule	France		Low enrichment	Operating	French CEA
EUREX	Italy	†	High enrichment	Completion expected in 1965	Italian CNEN
Allis-Chalmers, CNEN	Italy	15–30 kg/day	ThO_2-UO_2	Completion expected in 1964	Italian CNEN
Japanese	Japan	0.7–1 ton/day	Low enrichment	Beginning design	Japan Atomic Fuel Co.

*Capacity given is for low-enrichment fuels.
†Capacity is three to six Materials Testing Reactor (MTR) type elements per day.

Testing programs related to shipping containers, including impact testing and fire testing of models and full-scale casks, are described.

It is apparent from the papers presented that the problem of safe and economical transportation of radioactive materials, such as spent fuel elements, is complex and difficult. If cost was of no concern, acceptable casks could be designed without difficulty by limiting the size of the cask and the amount of irradiated fuel contained therein. However, the important function of the cask designer is to produce the most economically acceptable design. In general, when a sufficient amount of fuel is available for shipment, capital costs and operating costs are reduced by increasing the amount of fuel in the cask. At present, an upper limit of 75 to 100 tons for the loaded cask weight is imposed by the available handling and shipping facilities, although this limit may be extended in the future. It is for these large casks that severe technical and engineering problems arise.

In order to minimize cost and at the same time have a high degree of confidence in compliance with the regulations, it is important to have data and methods for reliable prediction of the behavior of fuel and cask. For several requirements of the proposed AEC regulations, 10 CFR Part 72, engineering knowledge is at present inadequate. Much more experimental information is needed on damage from impact, characteristics of the standard fire test, release of activity from fuel at elevated temperatures, and expected fuel temperatures after loss of coolant.[4]

A study at Oak Ridge National Laboratory (ORNL) on damage to prototype casks resulting from impact loading was recently completed.[5,6] Drop tests were made on eight model casks built for the program. Damage to the casks was slight for drops of 15 ft and under, except on corner and "piston" drops. When the 1.4-ton model casks were dropped onto a 2-in. piston, the steel shell was penetrated for all drops of 2 ft and above. From tests performed at ORNL and at Franklin Institute in Philadelphia, it has become evident that there is a direct correlation between the deformation of an exact scale model and that of a full-scale cask when impacted under identical conditions. The drop tests indicate that the AEC criteria on cask damage under accident conditions are reasonable, although it will be difficult to meet the proposed piston-drop requirement.

Since casks should be designed so that the radioactive decay heat can be removed without seriously damaging the fuel even in the absence of liquid coolants, experimental data and methods of predicting heat-transfer rates from the spent fuel to the inner wall of air-filled casks have been obtained by Watson at ORNL.[7] A calculational procedure presented in the report based on transfer of heat by radiation was

shown to give good predictions of the measured temperature distributions for the conditions likely to be of interest in shipping spent fuels (closely packed bundles with high heat-generation rates and temperatures).

In another study at ORNL, an analysis of the cost of shipping spent fuel elements from southern California to Hanford, Wash. (1175 miles), and from Italy to southern California was made.[5] The fuel was assumed to be natural uranium irradiated to a level of 8500 Mwd/metric ton. Truck shipment of a cask filled with 13 fuel elements and weighing 24.5 tons was estimated to cost $0.60 per mile, based on Hanford experience with similar shipments. On this basis the cost of shipping spent fuel the 1175-mile distance would amount to $1.30 per kilogram of uranium when shipments are made at a frequency corresponding to a fuel discharge rate of 3 tons of uranium per day. This cost includes transportation, handling, and cask depreciation and assumes that a load of this magnitude would be approved by the states through which the fuel would be hauled.

The corresponding cost of shipping the same distance by rail varied with the size of the shipment, as shown in the following tabulation:

Elements per cask	Cask weight, tons	Cost, $/kg
13	24.5	2.23
26	43.5	1.86
48	75.0	1.67

In comparison, the predicted cost range in shipping similar fuel 6000 miles round trip from western Massachusetts to Hanford, Wash., based on the cost of shipping spent natural-uranium fuels from Chalk River to Savannah River, is $1.53 to $2.56 per kilogram of uranium. The cost of shipping spent fuel 8500 miles from Italy via the Panama Canal to southern California was estimated to be $1.25 per kilogram of uranium. This is considerably less than the cost of ocean shipment to New Orleans and overland by rail to southern California (which was estimated at $3.50 per kilogram of uranium), even though the distance is shorter. Estimates of the costs of ocean shipment were based on costs of time-chartering a Liberty ship by the year and making approximately five round trips a year.[5]

It should be noted, however, that the above costs do not include property insurance coverage. Also, the new regulations governing the passage of irradiated nuclear fuel through the Panama Canal include a provision that no vessel carrying spent fuel may use the Canal without adequate provision for indemnity covering liability and loss to the United States comparable in scope to the protection afforded by Price-Anderson indemnification.[1]

Another aspect of the transportation problem is described in a report from Johns Hopkins University on the highway transport of radioactive materials.[8] The accident experiences of large motor carriers in the United States were studied in order to devise suitable measures to reduce the accident risk to truck shipments of highly radioactive materials. There appears to be considerable advantage in rerouting shipments away from or delaying shipments over crowded two-lane roads in winter. It was recommended that a report system be developed for the purpose of detecting those instances of unusually high risk where operational controls would be effective and that research be concentrated on the design of containers and vehicles that are capable of withstanding the forces encountered in highway accidents.

A literature search containing a total of 276 references to report and published material on shipping and storage of radioactive materials has been issued. An additional 32 references to engineering drawings are included.[9]

Fuel-Processing Economics

Thorium Fuel Cycle

A compilation of papers presented at a symposium on the thorium fuel cycle at Gatlinburg, Tenn., in December 1962 has become available.[10] A number of the papers from this symposium are reviewed in other sections of this issue of *Reactor Fuel Processing*. The objectives and plans for U. S. thorium fuel-cycle programs was discussed by Pittman of the AEC's Division of Reactor Development.[11] It now appears that the principal near future application of the thorium fuel cycle will be in thermal nonbreeding reactors where the relatively high conversion ratio will reduce fissile fuel makeup costs and allow longer fuel life without excessive fuel loading and reactivity control requirements. These objectives are be-

ing sought in conjunction with water-cooled and -moderated reactors, the spectral shift reactor, the all-ceramic gas-cooled graphite-moderated reactor, and the molten-salt converter reactor.

One objective of the thorium program is to provide, or assure, adequate development of thorium recycle technology and to ultimately remove the necessity of bred fuel buy-back guarantees by the AEC. Probably the most difficult problem is the one of developing an economical method for processing irradiated fuel and refabricating the fertile and fissionable material into fuel elements suitable for reuse in power reactors. This problem is made particularly challenging by the fact that the recovered thorium and U^{233}, even after removal of the fission products, rapidly become radioactive owing to daughter products of U^{232}.

Four different approaches to the problem of radiation from the U^{232} daughter products are being considered. First is a system involving high decontamination and direct fabrication. In this system, fuel is chemically processed, to remove essentially all fission products and to produce separate uranium and thorium product streams. The thorium product stream is stored 10 to 15 years before recycling to allow decay of the Th^{228}, the first daughter of the U^{232} decay series. The uranium product stream is again cleaned up chemically immediately before fabrication begins. Direct fabrication methods can be used if the work proceeds promptly and if measures are taken to decontaminate routinely and adequately all unshielded process equipment. An initial demonstration of this basic process will be conducted by ORNL. Additionally, one industrial group, the Babcock & Wilcox Co., is constructing a developmental facility and is planning to use this process in commercial nuclear activities.

The second system involves high decontamination and remote fabrication. This system is similar to the first in that separation of thorium and U^{233} would be carried out in a conventional chemical separation plant. However, no special chemical cleanup of the U^{233} prior to fabrication would be used, and no long decay period prior to recycling the thorium would be employed.

The third system involves partial decontamination and remote fabrication. Only one cycle of solvent extraction is planned, giving a level of decontamination that corresponds approximately to the level of activity which will be present in recycled U^{233} owing to ingrowth of daughter products. Chemical processing and fuel refabrication both require shielding and can both be carried out in a single building. A plant design based on this concept has been prepared by the Allis-Chalmers Mfg. Co. for the Italian National Committee for Nuclear Energy, and construction has been initiated. Plans have been made to furnish the initial Elk River reactor fuel loading for demonstration purposes in this plant.

The fourth system involves little or no decontamination and remote fabrication. This system is of potential interest in circumstances in which accumulation of fission-product poisoning is relatively unimportant and prompt processing for low fuel inventory is relatively important. Atomics International has been engaged in developments related to this concept.[11]

A paper describing the Italian plant, designed by Allis-Chalmers and using the third system mentioned above, was presented at the symposium by Davidson and others.[12] The plant, known as PCUT, is described in Sec. II of this issue. It is designed for a capacity of 15 kg of thorium-uranium oxides per day, but minor additions to the plant will permit processing at a capacity of 30 kg per day. In discussing the economics of the plant and the process, the authors state that preliminary studies have been made of a scaled-up version of the PCUT plant which would be capable of processing the spent fuel from one or two 300-Mw(e) boiling-water reactors on the same site as the processing plant. The fuel-cycle costs for such an integrated station with the thorium cycle were shown to be lower than that of a similar reactor operating on low-enrichment uranium with the spent fuel returned to the AEC.

The authors give the following reasons for the favorable costs in this system. The small integrated plant essentially eliminates all shipping costs as well as the costs of conversion of UF_6 to uranyl nitrate, the conversion of uranyl nitrate to UF_6, and the conversion of plutonium nitrate to metal. In addition to those costs that are eliminated completely, the processing steps remaining are simplified so that the effect of low plant capacity is less important; for example, rather than three cycles of solvent extraction to obtain full fission-product decontamination, only one cycle is used. The small size of the full-scale plant also permits a maintenance and service technique based on

rack-mounted units with quick-disconnect couplings. The design of the plant to serve a single reactor also results in a significant saving. A large central plant, even a 1 ton/day plant, would have to be designed for several different types of fuels. This requires a multiplicity of head-end and dissolving facilities, which are expensive.

A more subtle cost saving in the small plant results from the lower rate of return required of the invested capital. Since the plant has a guaranteed market for the life of the reactor, the capital investment in the processing plant need only be returned at the rate of the reactor itself, rather than at a rate approximately twice this, which would be reasonable for an independent central processing plant.

Finally, according to some estimates, the utilities and services that must be provided account for about 25% of the cost of processing in a 1 ton/day plant. However, in an integrated station, the incremental cost for utilities is very low.

The major cost of the processing cycle is not the chemical processing itself but is the refabrication of the fuel assemblies. For conventional fuel assemblies, the refabrication is a piecework job requiring jigs and fixtures and trained personnel. This cost is not strongly influenced by the capacity. In either the plutonium or the thorium cycle, the recycling of fissile material requires at least semiremote refabrication owing to the alpha activity. In the PCUT plant, additional protection against gammas is necessary during fuel fabrication. If the cost difference between the construction and operation of a remotely operated hot cell and a semiremotely operated glove-box line is not significant, then the PCUT plant system appears advantageous. This will only be known after further experience is acquired.[12]

Uranium Fuel Cycle

In conjunction with studies being carried out at ORNL on the use of large nuclear reactors for the desalinization of sea water, a study was undertaken to estimate the fuel-cycle costs for several nuclear fuels over a wide range of reactor sizes corresponding to fuel-processing rates of 1 to 30 short tons of uranium per day.[5] The fuels studied were (1) natural-uranium Zircaloy-clad UO_2, (2) the same fuel elements with the irradiated elements discarded rather than processed, and (3) depleted uranium and recycled plutonium so that UO_2–0.5% PuO_2 replaced the natural uranium in the above elements.

Table I-2 ESTIMATED FUEL-CYCLE COSTS FOR NATURAL-URANIUM FUEL[5]

Function	Case A (natural uranium)			Case B (Pu throwaway)	
	1 ton U per day ($/kg U)	10 tons U per day ($/kg U)	30 tons U per day ($/kg U)	10 tons U per day ($/kg U)	30 tons U per day ($/kg U)
Cost of U_3O_8	13.00	13.00	13.00	13.00	13.00
Refinery, U_3O_8 to UO_3	5.91	0.79	0.48	0.79	0.48
Cost of Zircaloy	4.50	3.58	3.40	3.58	3.40
Cold fuel shipment	0.05	0.05	0.05	0.05	0.05
Fabrication plant	8.04	2.50	1.04	2.50	1.04
Rejection, 5% of above, excluding ore	0.90	0.34	0.25	0.34	0.25
Subtotal, fuel-element cost	32.40	20.26	18.22	20.26	18.22
Processing	25.27	3.86	1.94	1.00	1.00
Pu loss at 0.25%	0.07	0.07	0.07		
Shipping irradiated fuel	1.32	1.27	1.27		
Inventory costs, reactor plus fuel cycle	4.17	3.50	3.15	1.43	1.30
Subtotal	63.23	28.92	24.65	22.69	20.52
10% for uncertainty	6.32	2.89	2.46	2.27	2.05
Total	69.55	31.81	27.11	24.96	22.57
Pu credit at $6.70/g and 4 g Pu per kg U	−26.80	−26.80	−26.80		
	43.55	5.01	0.31	24.96	22.57

In all cases the plant units were considered to have a single purpose; i.e., they were designed for and operated on a single type of fuel at a particular throughput. The ground rules were: capital charges at 7.7%/year; municipal financing; inventory charges at 5.5%/year; natural uranium in ore concentrates at $13/kg; and depleted uranium from diffusion-plant tails at $2.50/kg.

The results, indicating fuel-cycle costs dropping from $43.55 to $0.31 per kilogram of uranium, are shown in Tables I-2 and I-3. The tabulated cost for the uranium refinery at 1 ton/day is probably high because the costs for large plants were extrapolated to costs for plants below a practical size. The value of plutonium produced and sold was taken as $6.70/g. For the "throwaway" case, no processing of irradiated fuel was done, and the spent fuel was stored under water in a constantly expanding basin near the reactor. For the plutonium-recycle case, the preparation of reactor-grade UO_2-PuO_2 was based on a large scale-up of a few successful laboratory sol-gel process experiments. Twelve inches of concrete shielding and remote operation were provided for the sol-gel and fuel-fabrication steps.

The results of the study indicate that natural-uranium fuels have the lowest fuel-cycle costs for this application and that unit costs are greatly reduced by an increase in production throughput for all fuels considered.

Table I-3 ESTIMATED FUEL-CYCLE COSTS FOR PLUTONIUM RECYCLE CASE[5]

	Dollars per kilogram of U at 85% on-stream efficiency		
	1 ton U per day	10 tons U per day	30 tons U per day
UF_6 to U_3O_8	0.77	0.23	0.15
U_3O_8 to UO_3	2.08	0.54	0.39
UO_3 to UO_2-PuO_2	3.78	1.20	0.77
Subtotal UF_6 to UO_2-PuO_2	6.63	1.97	1.31
Fabrication	18.35	8.60	
Subtotal UF_6 to element	24.98	10.57	
Processing	26.19	4.10	2.07
Shipping	1.90	1.82	1.82
UF_6 feed	2.50	2.50	2.50
Total cycle without inventory	55.57	18.99	

Radiochemical Plant Safety

The hazards associated with a large radiochemical plant for either fuel processing or radioisotope source production may exceed those of a nuclear reactor. A comprehensive survey of the hazards associated with U^{233} and Pu^{239} fuel fabrication and radioisotope processing plants has been made at ORNL.[5]

Radiochemical plants are normally designed such that in the event of an accident one or more containment systems operate to limit the release of radioactive material to the environment (contained accident). The simultaneous occurrence of (1) a fire or explosion that disperses the maximum amount of material, (2) a containment failure, and (3) unfavorable meteorological conditions has such an extremely low probability of occurrence as to be deemed incredible. Even so, a study of these accidents is valid in order to obtain an upper limit on liability. The results of this study are summarized in Table I-4, which presents the potential economic loss from the worst contained and worst uncontained accidents in Pu^{239}, Sr^{90}, and Pu^{238} fabrication plants. The worst uncontained accident in such plants would possibly result in billions of dollars of economic loss due to damage to the surrounding land and population. The

Table I-4 POTENTIAL ECONOMIC LOSS IN WORST CONTAINED AND WORST UNCONTAINED ACCIDENTS[5]

Type of plant	Worst contained accident		Worst uncontained accident	
	Release to atmosphere	Potential economic loss	Release to atmosphere	Potential economic loss
Pu^{239} fuel fabrication	40 g (2.5 curies)	$\$3 \times 10^6$	4 kg (250 curies)	$\$4 \times 10^8$
Sr^{90} source fabrication	220 curies (1.5 g)	2×10^7	50,000 curies (350 g)	5×10^9
Pu^{238} source fabrication	2.2 g (37 curies)	5×10^7	2 kg (34,000 curies)	5×10^{10}

ground rules and assumptions made in evaluating the potential economic loss are given in the reference report.

Although there is not sufficient radiochemical plant operating experience to establish a probability for a major accident, in general, the frequency and severity of accidents in such plants have been lower than in the related chemical industry. A review of the accident experience does indicate that in most cases serious accidents result from an unforeseen combination of several independent circumstances and that relatively minor accidents can start a series of events that result in a major accident.

(A. A. Jonke)

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Section

II

Reactor Fuel Processing

Research and Development on Aqueous Processing

The principal areas now involved in work on the development of aqueous fuel processing appear to be those concerned with the preparation of nonmetallic fuels and the application of solvent-extraction techniques.

Preparation of Fuel for Processing

Methods of fuel preparation include mechanical or chemical decladding, other means of chemically attacking cladding or matrix material, and partial or complete dissolution.

Mechanical Processing Methods

The mechanical dejacketing of liquid-metal-bonded nuclear fuels is the subject of a comprehensive paper by Watson.[1] Because this work has been reviewed in previous issues of *Reactor Fuel Processing*,[2,3] the report is only mentioned here to bring it to the attention of the reader. The report is a valuable contribution because of its completeness and the excellent reference list that is included in the report.

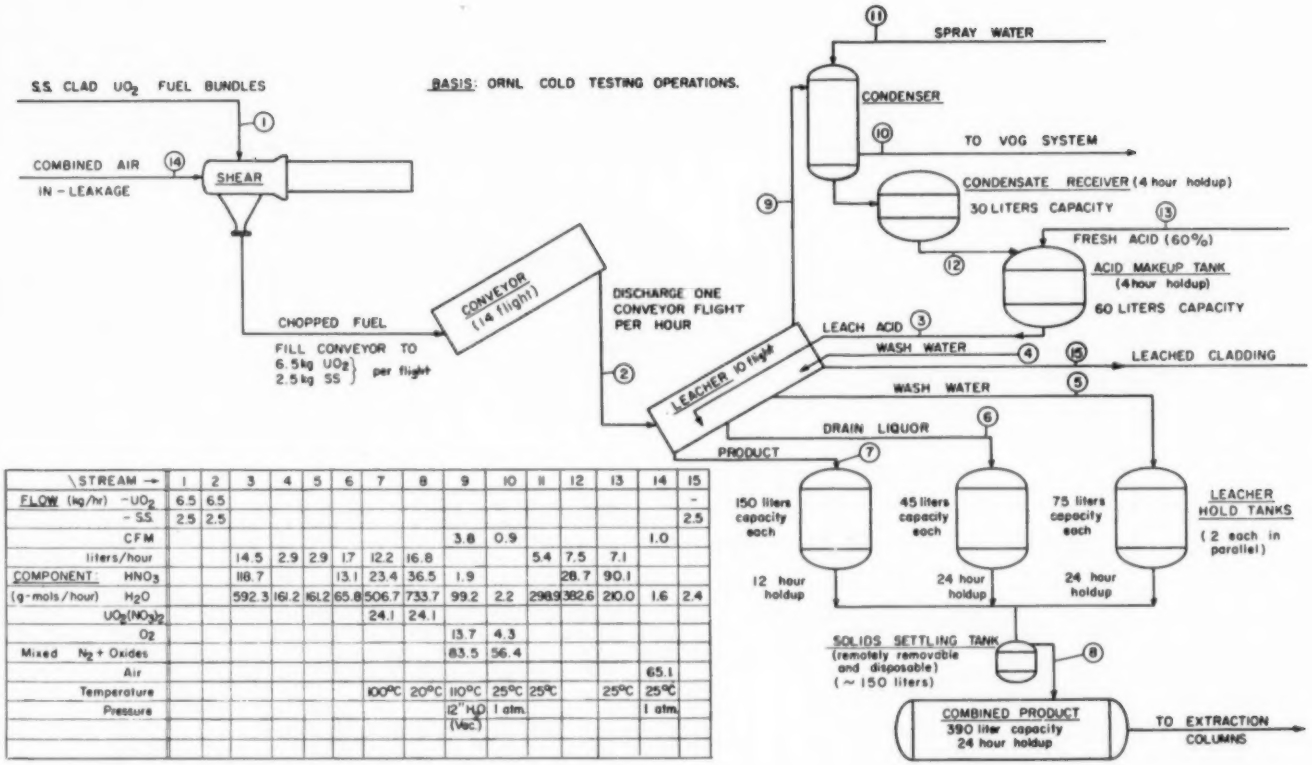
Buckham and P'Pool[4] have reported on a conceptual study of a system for the demonstration of the chop-leach process using actual reactor fuels. The process involves the shearing of bundles of fuel tubes into short pieces and leaching these pieces with hot acid to dissolve selectively the urania or thoria fuel from the stainless-steel or Zircaloy cladding. Figure II-1 shows the preliminary flow sheet studied, and Table II-1 lists the fuels that might be used in the demonstration of the process along with the characteristics of the fuels. In the same report, Pitkin presents detailed conceptual designs and cost estimates for the chop-leach facility.

Various locations for the demonstration facility at the Idaho Chemical Processing Plant (ICPP) are considered. Of the three plant concepts that were chosen for detailed study, the one that is believed to be the best choice would cost about $660,000 to install; however, this facility might not be the most convenient for operation and maintenance, since the equipment would be fitted into existing ICPP facilities. Detailed process steps, with the times required, are presented for some of the fuels listed in Table II-1. (D. M. Paige)

Oxidation of Graphite-Matrix Fuels

Among the fuel types planned or being considered for use in advanced gas-cooled reactors, such as the High-Temperature Gas-Cooled Reactor (HTGR) and the West German Pebble-Bed Reactor, are those consisting of coated ceramic particles embedded in a graphite matrix. The ceramic may be thorium or uranium oxide or carbide, and the coating may consist of pyrolytic carbon, alumina, or beryllia. Blanco and others, in a recent review[5] of process methods for coated-particle fuels, have reported on a technique including oxidation of the graphite followed by acid dissolution of the ash to prepare a feed for solvent extraction.

The combustion operation must be contained and also must be controlled to prevent reaching sintering temperatures for the ash. Sintering could not only reduce the rate of residue dissolution but might also complicate transfer operations. Oxidation studies were made in externally cooled nickel pipes 2 to 5 in. in diameter. In the larger unit, graphite was burned satisfactorily in 50% air–50% oxygen at a maximum rate of about 1.8 kg/hr with the production of a small amount of carbon monoxide. Solids in the cooled off-gas collected by sintered metallic filters included less than 0.2% of the uranium in



\STREAM →	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
FLOW (kg/hr) $-UO_2$	6.5	6.5													-
- SS	2.5	2.5													2.5
CFM									3.8	0.9				1.0	
liters/hour			14.5	2.9	2.9	1.7	12.2	16.8			5.4	7.5	7.1		
COMPONENT: HNO_3			118.7			13.1	23.4	36.5	1.9			28.7	90.1		
(g-mols/hour) H_2O			592.3	161.2	161.2	65.8	506.7	733.7	99.2	2.2	298.9	382.6	210.0	1.6	2.4
$UO_2(NO_3)_2$							24.1	24.1							
O_2									13.7	4.3					
Mixed N_2 + Oxides									83.5	56.4					
Air														65.1	
Temperature							100°C	20°C	110°C	25°C	25°C		25°C	25°C	
Pressure									12" H_2O (Vac.)	1 atm.				1 atm.	

Fig. II-1 Preliminary flow sheet for chop-leach process.[4]

Table II-1 CHARACTERISTICS OF POSSIBLE REACTOR FUELS FOR RADIOACTIVE CHOP-LEACH DEMONSTRATION[4]

	CETR*	Dresden†	Yankee‡	Elk River§	Hallam¶	N.S. *Savannah***	EBWR††
Fuel data							
Composition	2.8–10.8% UO_2-ThO_2	UO_2	UO_2	UO_2-ThO_2	U–10% Mo	UO_2	UO_2
Amount per assembly		124.6 kg of UO_2	19.8 kg of U	4.6% UO_2, 95.6% ThO_2	202 kg of U	222 kg of U	
Reactor loading	15,100 kg of Th, 1100 kg of U	52,600 kg of U	21,400 kg of U	171 kg of U^{235}, 3787 kg of Th	25,500 kg of U	7100 kg of U	
Initial enrichment	93% U^{235}	1.5% U^{235}	3.4% U^{235}	93.5% U^{235}	3.5% U^{235}	4.2–4.6% U^{235}	~3% U^{235}
Burnup	23,200 Mwd/metric ton of Th	12–15,000 Mwd/metric ton of U	8200 Mwd/metric ton of U	9500 Mwd/ton of U-Th	~7500 Mwd/ton of U	7400 Mwd/ton of U	
Pu produced		0.490 kg per assembly	~5000 g/ton of U		~0.600 kg per assembly	~2800 g/ton of U	
Bond	He			He	He and Na	He	
Tube data							
Material	304 S.S. (200 ppm B)	Zircaloy-2	304 S.S.	304L S.S. (640 ppm B)	S.S.	304 S.S.	S.S.
Outside diameter, in.	0.304	0.570	0.340	0.452	0.660	0.500	0.500
Wall thickness, in.	0.0205	0.033	0.021	0.020	0.010	0.035	0.015
Overall length, in.	102.25	116.75	95.0	65.1	182.0	69.0	62.0
Active length, in.	98.5	111.78	90.0	60.0	162.0	66.0	60.0
Assembly data							
Type	Square bundle in casing	Square bundle	Square array	Square bundle	Circular cluster	Square bundle	Box
No. of tubes	196	36	306	25	18	164	10
Overall dimensions, in.	5.7 by 5.7 by 137.75	4.4 by 4.4 by 134.3	7.61 by 7.61 by 111.25	3.5 by 3.5 by 81.68	4.4D by 249.25	8.7 by 8.7 by 76.5	3.88 by 3.88 by 88.0
Construction	Ferrules brazed between tubes; 56 bundle spacers at each end; Zircaloy-2 casing	Tie plates at ends; spacer plate at 3 segment joints	Bundle straps	Tubes welded to end grids and separated by 3 wire grids	Strips and/or spiral wrap wire for tube spacing; central solid rod	Slotted end fittings welded to frame at each end; handling knob welded to 0.563 in. OD by 0.375 in. ID shaft extending length of assembly	$4^5/_{64}$-in. S.S. side plates, spacer tubes, and/or clips
No. per core	120	488	76	148	~120	32	~144
Subassembly data							
No. per assembly			9			4	
No. of tubes			34			41	
Overall dimensions, in.						4.52 by 3.86 by 72.0	
Construction		Tube sheet	Ferrules brazed between rods			Tubes spaced by brazed ferrules; 15 of the peripheral rods are brazed into slotted end pieces at each end	
Shipping data							
Shipping preparations	Min. 120 days cooling	60–90 days cooling	100 days cooling	150 days cooling	Cooled 90 days; cleaned	30 days cooling; end adapters cut off	
Shipping carrier weight	70 tons	70 tons			~40 tons		
Carrier dimensions		7.5 by 6.5 by 14.0 ft	Octagonal, 5.858 ft across face by 12.75 ft		36 in. OD by 18 in. ID by 20 ft		
No. of assemblies per carrier		32	4				

*Consolidated Edison Thorium Reactor, Consolidated Edison Co., Indian Point, N. Y.
†Dresden Nuclear Power Station, Commonwealth Edison Co., Morris, Ill.
‡Yankee Atomic Power Station (cores 1 and 2), Yankee Atomic Electric Co., Rowe, Mass.
§Elk River Reactor, Rural Cooperative Power Associates, Elk River, Minn.
¶Hallam Nuclear Power Facility, Consumers Public Power District, Hallam, Nebr.
**Nuclear Merchant Ship *Savannah*.
††Experimental Boiling-Water Reactor (core 3), Argonne, Ill.

the charge, and the loss through the off-gas filter was less than 0.002%.

Extensive volatilization of ruthenium and cesium occurred in initial small-scale combustion studies with irradiated graphite fuel. In tests with irradiated uranium dicarbide–graphite-matrix fuel (0.1% burnup), over 40% of the ruthenium was volatilized at 800°C. With HTGR fuel samples irradiated to about 9000 Mwd/metric ton of uranium + thorium, 6-hr combustions in oxygen resulted in considerably greater volatilization of ruthenium at 1200°C than at 800°C, as shown in Table II-2.

Table II-2 VOLATILIZATION OF RUTHENIUM AND CESIUM DURING COMBUSTION OF GRAPHITE FUEL[5]

(Fuel: HTGR Type, Irradiated to 9000 Mwd/Metric Ton of Uranium + Thorium; Burned 6 Hr in Oxygen)

Combustion temp., °C	Fission-product volatilized, %	
	Cesium	Ruthenium
800	22–24	74
1200	67–84	97–98

The ashes produced from thorium-uranium fuel mixtures dissolved readily in a 200% excess of boiling 13*M* nitric acid containing 0.1*M* aluminum nitrate and 0.04*M* fluoride. If silicon carbide is present, the silica residue may retain a small fraction of the uranium.

Hydrolysis of Uranium Carbide Fuels

At Oak Ridge, studies reported earlier[6] on the hydrolysis of uranium and thorium carbides have been continued. It was noted that irradiation of uranium monocarbide to about 500 Mwd/ton (estimated surface temperature was 800°C) affected the hydrolysis of the material by water at 90°C (Ref. 7). Although similar amounts of gas were obtained from irradiated and unirradiated monocarbide, the gas from the irradiated material was about one-third hydrogen and two-thirds methane, whereas the gas from the hydrolysis of similar unirradiated pellets was about 10% hydrogen and 90% methane. Small amounts of higher hydrocarbons were produced in both cases. The gas from the irradiated material also contained somewhat more of the original carbon content than that from the unirradiated material. In later studies with much more highly irradiated material (5000–7000 Mwd/ton), the irradiated material was almost nonreactive with water at 80 to 90°C (Ref. 8). Reactivity of the highly irradiated material in mineral acids, however, appeared to be greatly accelerated. For example, dissolution of irradiated pellets in concentrated nitric acid was complete in 30 min as compared with 2 hr required for unirradiated pellets.

Hydrolysis of uranium monocarbide by sodium hydroxide solutions has also been examined at Oak Ridge.[9] As the caustic concentration was increased from 2*M* to 18*M*, the rate of reaction decreased and the amount of gas generated increased slightly. As with water hydrolysis, the gas was mostly methane with some hydrogen.

Dissolution of Zirconium Alloy in Hydrofluoric Acid

It is proposed to increase the capacity of the zirconium-uranium alloy fuel-processing system at the ICPP by converting the existing batch dissolver to a semicontinuous unit. The process, which is designed to accommodate alloys containing a few percent of highly enriched uranium in zirconium, with a cladding of Zircaloy, consists of dissolution in hydrofluoric acid and complexing of excess fluoride with aluminum to enable tributyl phosphate (TBP) extraction from a nitrate system. To ensure criticality safety, it is planned to maintain boron as a neutron poison in solution in the dissolving vessel at a concentration of about 4 g/liter. It is reported[10] that boron, added as boric or fluoboric acid, was not present in the small residues of tin or zirconium fluoride hydrolysis products from continuous dissolution. The presence of boron had no effect on the dissolution, adjustment, or extraction steps, except that a slightly higher fluoride concentration was needed to ensure stability of the dissolver product. Corrosion of Monel metal specimens in hot solutions typical of the dissolver product was at rates of the order of 1 to 2 mils/month in a 1600-hr test, whereas in a shorter test Carpenter-20 alloy corroded at a rate of less than 1 mil/month.

Corrosion of Dissolver Construction Materials

A recent Russian article summarizes extensive laboratory data on the corrosion of typical dissolver construction materials by acids suitable for dissolving a number of nuclear

fuels and cladding materials.[11] The data are explained on the basis of passivation theory and electrode potentials. The reagents considered are nitric, hydrofluoric, and sulfuric acids, and nitric acid containing small additions of fluoride; the materials evaluated include titanium-stabilized 18-8 stainless steel, Monel, copper, and 23% chromium–27% nickel ferrous alloy (X23N27M3D3T).

The article summarizes work on the corrosion of 18-8 stainless steel in boiling nitric acid by noting that, in the concentration range from 8*M* to 14*M* nitric acid, acceleration of corrosion is associated with the breakdown of the passive state. Sharply increased corrosion in dilute acid solution may result from contact with electronegative metals. This is illustrated in Fig. II-2, which shows a maximum at about 2*M* nitric acid in the curve for corrosion rate in the presence of mercury ions as a function of nitric acid concentration for stainless steel in contact with aluminum.

Considerable data are also reported for the corrosion of Monel metal and copper in hydrofluoric acid up to concentrations of 40% between 20°C and the boiling point. It is particularly noted that corrosion is most severe in the vapor phase, being generally an order of magnitude greater than that of specimens in the bulk liquid. The corrosion process appears to involve an oxidative depolarization and to be principally cathodically controlled.

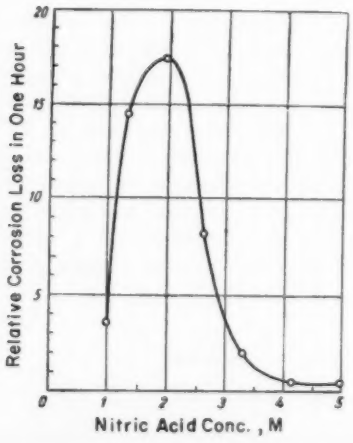


Fig. II-2 Velocity of corrosion of 18-8 titanium-bearing steel in contact with aluminum, in boiling nitric acid solutions containing 0.05% mercuric nitrate.[11]

Small additions of fluoride are observed to accelerate sharply the corrosion of stainless steel in nitric acid. The degree of agressiveness for a given amount of fluoride added appears to depend on the concentration of hydrogen ion in the solution. This is shown by the data in Fig. II-3, which indicates corrosion rates for titanium-stabilized 18-8 stainless steel in 2*M* to 14*M* nitric acid containing up to 0.12*M* fluoride. In 2*M* to 8*M* acid, the rate of corrosion increases roughly in proportion to fluoride concentration, but at higher acidities a maximum corrosion rate is reached for a given aciditity at 0.025*M* to 0.10*M* fluoride, beyond which corrosion decreases with increased fluoride concentration. As the acidity increases, the fluoride concentration for maximum corrosion is observed to decrease.

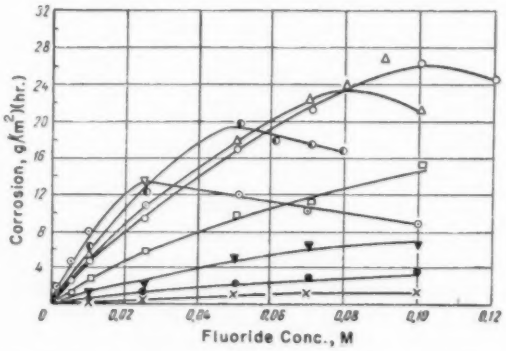


Fig. II-3 Influence of additions of ammonium fluoride on the corrosion of titanium-modified 18-8 stainless steel in boiling nitric acid solutions.[11] Nitric acid concentrations: ×, 2*M*; ●, 4*M*; ▼, 6*M*; □, 8*M*; ○, 1*M*; △, 12*M*; ◐, 12.5*M*; ⊙, 14*M*.

In corrosion studies on the alloy X23N27-M3D3T in boiling 6*M* sulfuric acid, it was shown that the rate of corrosion could be reduced by the addition of oxidants, e.g., 0.2 g of ferric ion per liter. Ferric ion was observed to effect a marked change in the potential of the alloy relative to the solution and to afford cathodic protection. (C. E. Stevenson)

Solvent-Extraction Separations Processes

Some time ago, certain of the papers presented at a symposium on solvent-extraction

chemistry held at Gatlinburg, Tenn., October 23–26, 1962, were reviewed.[12] Six of these papers (and three that were not previously reviewed) have recently appeared in *Nuclear Science and Engineering*.[13–18]

Process Condition Studies

Plutonium Polymerization

The hydrolysis and subsequent polymerization of tetravalent plutonium ions may be an important factor in defining the preparation and handling of solvent-extraction process feed and product solutions, since polymeric plutonium is not extracted by the usual solvents, nor is it sorbed on ion-exchange resins. Precipitation of the polymer can also result in serious product losses and criticality problems. Costanzo and Biggers[19] have reported the results of a very significant spectrophotometric study of both polymerization and depolymerization of plutonium ions as functions of temperature, acidity, and the presence of other electrolytes.

Studies of the polymerization of tetravalent plutonium are complicated by the observation that disproportionation and nitrate oxidation can occur simultaneously. The rates of these reactions are all dependent on acidity. Although the mechanism of the polymerization reaction is not known, it can be represented by the following expression:

$$y\mathrm{Pu}^{4+} + (x + 2y)\ \mathrm{H_2O} = (\mathrm{PuO_2})y \cdot x\mathrm{H_2O} + 4y\mathrm{H}^{+}$$
Polymer

The effect of acidity on the Pu(IV) polymerization rate at 25°C in nitric acid was studied for solutions containing 2.2 g of plutonium per liter. As shown in Fig. II-4, the rate of polymerization is more rapid at lower acidity and is very sensitive to acidity in the range 0.04*M* to 0.15*M* nitric acid.

The effect of temperature in accelerating the rate of tetravalent plutonium polymerization at the above plutonium concentration in 0.075*M* nitric acid was quite pronounced as observed from studies made at 25, 50, and 75°C.

The disproportionation reaction, although it also occurs rapidly, is readily reversible so that at 50°C over 90% of the plutonium is found in the polymer form after a few hours, compared to about 50% at 25°C. At 75°C, although the polymer concentration reaches an equilibrium level more rapidly than at 50°C, the fraction found as polymer is slightly lower, presumably due to the greater fraction converted to the hexavalent form by nitrate oxidation.

The effects of uranyl nitrate, aluminum nitrate, and sodium nitrate, and of fluoride, on the kinetics of polymer formation were also determined at low acidities and elevated temperatures. With high concentration of nitrate salts, the polymer precipitated to a considerable extent.

Freshly prepared plutonium polymer can be depolymerized fairly rapidly in strong nitric acid solution at 25°C. Half-times for conversion of polymer ranged from 20 hr at 1.0*M* nitric acid to 1.2 hr at 10*M* acid. Aged polymer is converted much more slowly, but the process is accelerated in the presence of aluminum nitrate or of fluoride ion at low concentrations.

TBP Solvent Deterioration

During a recent aluminum alloy fuel-processing run at the ICPP, some interesting data were obtained on the content of TBP decomposition products in various extraction process streams.[20] The data were obtained for the first extraction cycle in which the solvent used was

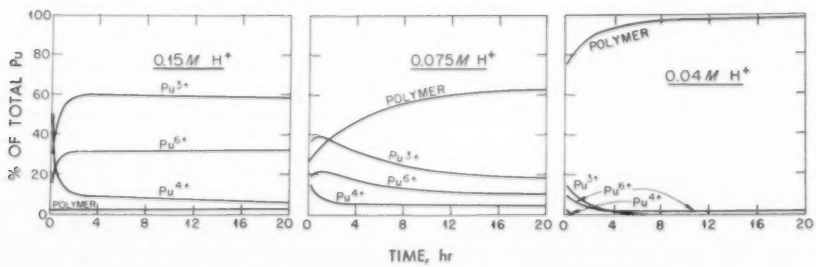


Fig. II-4 Effect of acidity on the rate of polymerization of Pu(IV) in nitric acid[19] at 25°C.

3.25% TBP and the aqueous phase was an acidic aluminum nitrate solution. In the first-cycle extraction column, rates of generation of dibutyl phosphate (DBP) were in the range 13 to 26 mg of DBP per liter of aqueous phase. Twice as much DBP left the extraction column in the organic as in the aqueous phase, the extraction column raffinate concentration ranging from 5 to 9 mg of DBP/liter.

In the stripping column, DBP distribution also favored the organic phase. Concentrations in the aqueous product ranged from 3 to 7 mg of DBP/liter, and in the organic raffinate they ranged from 11 to 25 mg of DBP/liter. No significant amount of DBP appeared to be generated in or to leave the first-cycle product evaporator. From analyses of one set of samples, it appeared that some precipitation might have occurred in the evaporator.

The solvent before being recycled is washed in mixer-settlers with dilute nitric acid and sodium carbonate. About 80% of the entering DBP was removed from the organic raffinate in this process. Recycled solvent contained 2 to 5 mg of DBP/liter. The stripping column product solution is washed with the hydrocarbon diluent in another mixer-settler unit; the hydrocarbon removed 90% of the residual TBP from the aqueous phase and very little of the DBP.

Study of these data suggested the desirability of adjusting process conditions to minimize TBP decomposition in the first-cycle extraction column in order to secure the optimum zirconium decontamination factor. Another desirable modification might be to wash the first-cycle product prior to evaporation in order to eliminate DBP from the first-cycle product evaporator.

Fission-Product Behavior in TBP Extraction

An extensive review article by N. E. Brezhneva and others has recently appeared in the Russian journal, *Atomnaya Energiya*, on the extraction separation of zirconium, niobium, and ruthenium in TBP systems.[21] Distribution data for these elements are given for undiluted TBP and 40% TBP in a hydrocarbon diluent in contact with dilute to concentrated nitric acid; the effects of peroxide and oxalate complexing are also illustrated as applied to zirconium and niobium extraction. A discussion of the significance of the nitrosyl compounds of ruthenium is also given along with procedures for the concentration of this element by carrier precipitation on sulfides of nickel and copper. In general, the work reported corresponds to the results of similar work carried out some time ago in this country and in the United Kingdom. There appears to be little novelty in either the data or the conclusions.

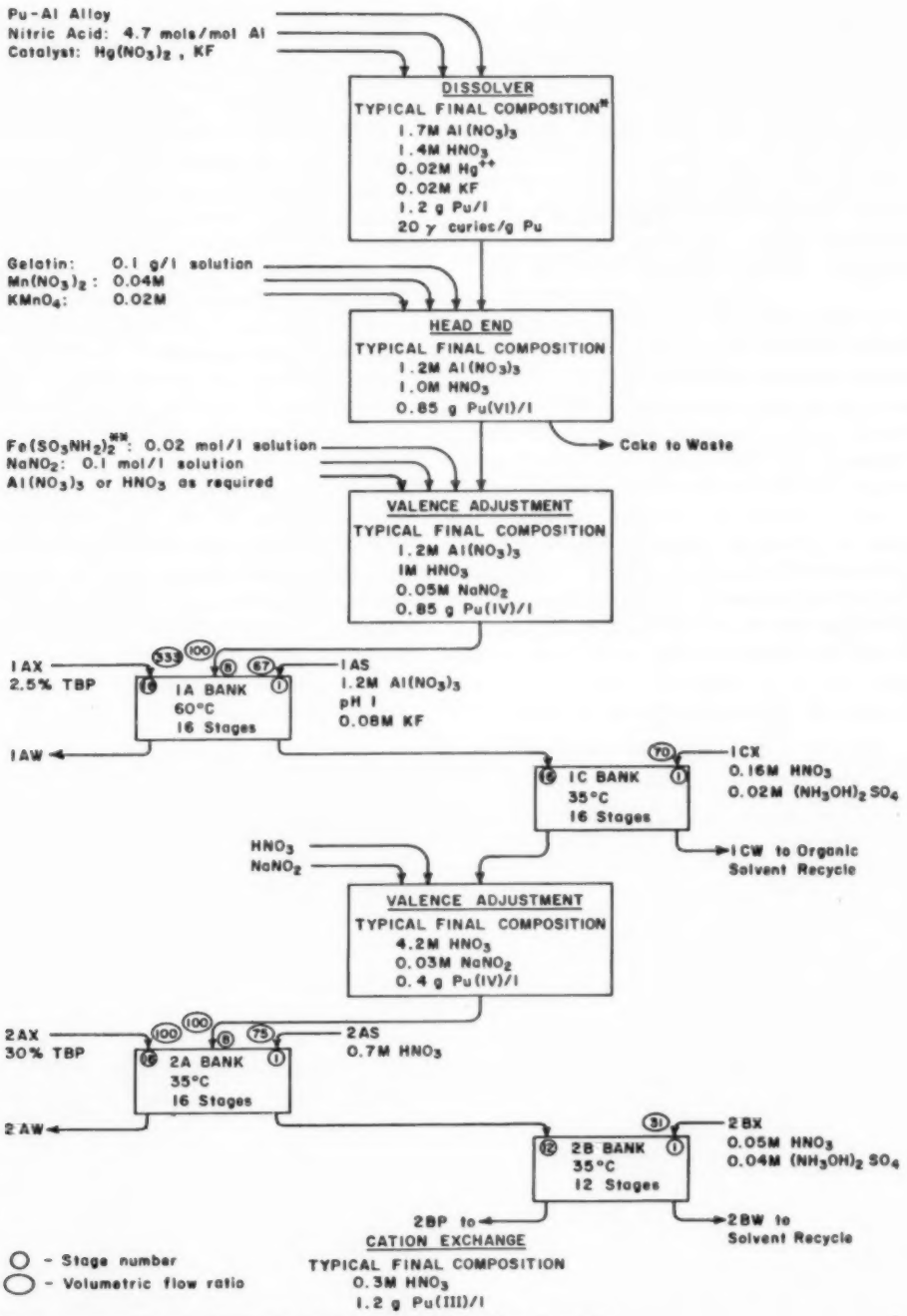
TBP Process for Aluminum-Plutonium Fuel

Alloys of plutonium with aluminum, containing minor quantities of plutonium, have been much used for the production of research quantities of transplutonium isotopes and higher plutonium isotopes by irradiation in high-flux reactors. One such alloy containing 7% plutonium was used to produce higher plutonium isotopes for the Plutonium Recycle Test Reactor (PRTR) at Hanford. Recovery of the plutonium was accomplished in the enriched-uranium processing facilities at the Savannah River Plant by a TBP process developed especially for this purpose. Development studies and a few observations resulting from the processing run were recently described by Schlea and others of the Savannah River Laboratory.[22]

A flow sheet for the process used is shown in Fig. II-5. It is a conventional two-cycle TBP extraction process which incorporates dissolution in dilute nitric acid containing mercuric ion and fluoride and which has valence adjustments with ferrous sulfamate and nitrite to maintain plutonium in an extractable condition. The development of the dissolution process has been discussed earlier.[23] Since the fuel alloy contains a significant amount of silicon, the dissolver solution is clarified by gelatin treatment. A manganese dioxide precipitation was also used as a head-end fission-product scavenging operation, and the dissolver solution was centrifuged before adjustment and extraction. The second solvent-extraction cycle was identical to the second plutonium cycle of the Purex uranium fuel process as carried out at Savannah River.

In miniature pilot-plant tests, the process gave adequate recovery of plutonium (loss was less than 1%). A gross gamma decontamination factor of 10^6 was achieved.

In the initial operation of the process in plant facilities, there was a loss of about 10% of the plutonium to the aqueous waste from the first cycle. This was later found to result from the failure of nitrite treatment to reduce Pu(VI) to Pu(IV). After the valence adjustment was changed



* If concentrations are lower, the solution is evaporated after dissolving.

** $Fe(SO_3NH_2)_2$ was not used in the laboratory tests, but was included in plant operations.

Fig. II-5 Flow sheet of the plutonium recovery process used for treatment of plutonium-aluminum alloy.[22]

to a two-step procedure involving reduction to Pu(III) with ferrous sulfamate, followed by oxidation to Pu(IV) with nitrite, losses of plutonium in the plant operation were less than 1%.

(C. E. Stevenson)

Plant and Equipment Design and Operation

One of the disadvantages of complete remote maintenance in a fuel-processing plant has been the large volume of space required for equipment. A recent installation at Hanford has demonstrated a much more efficient use of volume by "package" installation of two pulse columns, two pulse generators, two tanks, three sample pots, and a forest of remote connectors or jumpers in a space originally intended for a single column and pulse generator.[24] The space is J-2 canyon position (14 by 14 by 39 ft high).

The equipment is to be used for neptunium recovery as shown in Fig. II-6. The J-cell package was to be remotely movable into and out of the cell. Equipment subject to mechanical failure or process obsolescence was to be remotely removable from the package; this included pumps, agitators, jets, valves, flowmeters, and control instruments. Although small pulse generators of the Hanford design are considered to be trouble free, they were made remotely replaceable as an added precaution. The pulse column cartridges were designed for remote replacement for added process flexibility.

The report describes in some detail the design and construction of the package and contains a number of illustrations of various components of the package.

The recent publication of the Proceedings of the Thorium Fuel Cycle Symposium included several papers of interest covering plant designs. Two of these papers are reviewed below.

An Allis-Chalmers design group together with the members of the Comitato Nazionale per l'Energia Nucleare (CNEN)[25] present a design for a complete processing plant, known as the PCUT plant, to process Elk River reactor fuel. The facility has been designed to permit future conversion for the processing of thorium loadings of the SENN reactor now under construction near the Garigliano River in Italy. The PCUT

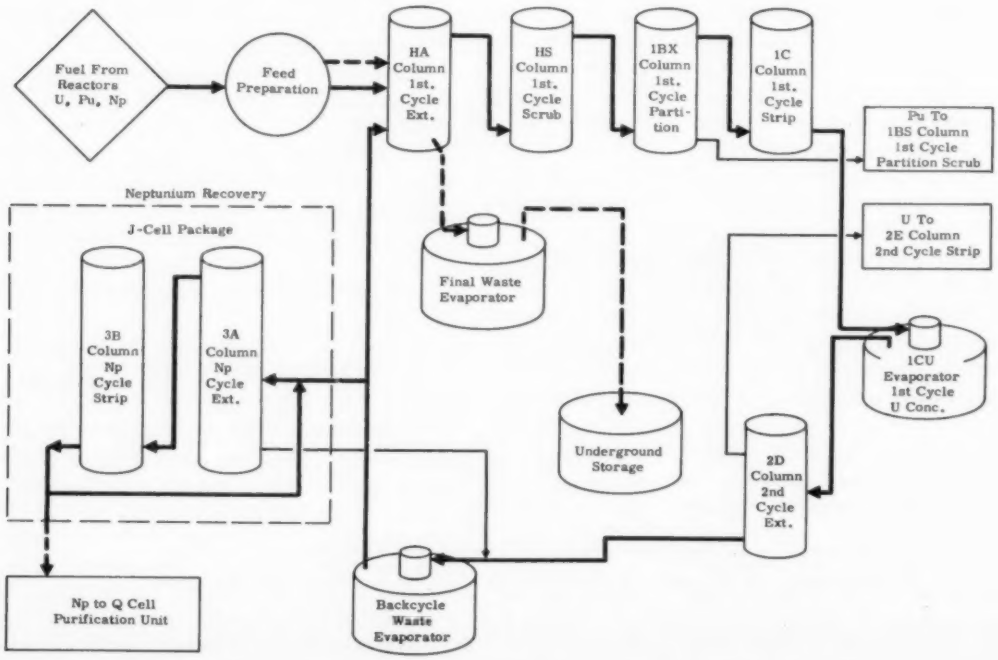

Fuel From Reactors U, Pu, Np
Feed Preparation
HA Column 1st. Cycle Ext.
HS Column 1st. Cycle Scrub
1BX Column 1st. Cycle Partition
1C Column 1st. Cycle Strip
Pu To 1BS Column 1st Cycle Partition Scrub
U To 2E Column 2nd Cycle Strip
Neptunium Recovery
J-Cell Package
Final Waste Evaporator
3B Column Np Cycle Strip
3A Column Np Cycle Ext.
1CU Evaporator 1st Cycle U Conc.
Underground Storage
2D Column 2nd Cycle Ext.
Np to Q Cell Purification Unit
Backcycle Waste Evaporator

Fig. II-6 Continuous neptunium recovery, Purex process.[24]

plant will be built by an Italian civil contractor near Policoro in southern Italy with startup scheduled in 1964.

The process involves several chemical and mechanical processes carried out remotely, not only because of fission-product activity, but because of the radioactivity associated with U^{232} and Th^{228}. Fifteen kg of thorium-uranium enriched up to 10% in U^{233} can be handled per day. Minor additions to the plant will allow the capacity of the plant to be increased to 30 kg of thorium-uranium per day.

The complete processing sequence is shown in Fig. II-7. The fuel elements ($81\frac{5}{8}$ in. long by $3\frac{1}{2}$ in. square) weigh 86 lb each and consist of stainless-steel tubes filled with ceramic pellets. The fuel element is first disassembled under water leaving fuel-bearing rods but not exposing the fuel.

The rods are chopped by a hydraulically operated shear into short segments. These segments fall directly into the dissolver which uses nitric acid but which leaves the stainless steel undissolved. One cycle of mixer-settlers is used to separate the thorium and uranium from the fission products. Only one cycle is planned since further processing work is done completely by remote control.

Formic acid and urea are added to the adjusted dissolver solution; the mixture is heated (60°C) and passed through a platinum-alumina pellet catalyst bed. This reduces the uranium and allows both uranium and thorium to be precipitated with oxalic acid. The precipitate can be removed by centrifuging.

After the material is calcined to the oxides, it is passed through a Mikro-Pulverizer and is blended with water; then an organic extrusion aid is added, and finally the material is extruded into 91 cm length. These rods are air dried, cut to length, sintered at temperatures up to 1700°C, and ground (centerless grinder) to required size.

The finished pellets are loaded into new tubes under a vacuum, and the tubing is sealed by welding in a helium atmosphere. The completed fuel rods are heated in a vacuum chamber that is connected to a helium leak detector. The he-

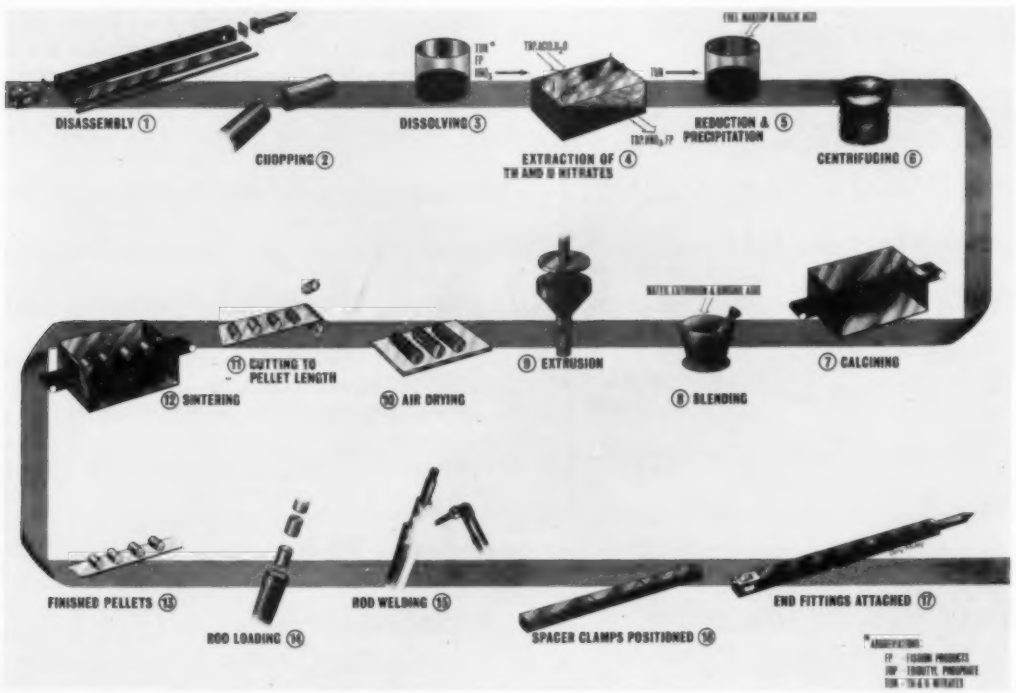


Fig. II-7 Processing sequence.[25] (Courtesy of Nuclear Power Division, Allis-Chalmers Mfg. Co.)

lium in the fuel rods ensures a positive test of the integrity of the rods. Bundles of 25 rods are assembled and fitted with spacer clamps, after which the end pieces are pressed into position. Specially designed snap rings lock the rod bundles to the end pieces and obviate further remote welding, which is complicated and difficult.

The fuel-element assembly machine holds five separate components in proper alignment and slides them together until snap rings lock into place. This eliminates welding or bolting in the assembly cell.

The operations are carried out in two shielded cells: a hot cell for high activity and a warm cell involving lower levels of activity. The hot cell is 35 ft long, $11\frac{1}{2}$ ft wide, and 14 ft high. The cell makes use of plug-in racks. Figure II-8 shows a model of the solvent-extraction rack. These racks can be removed remotely to a decontamination cell and repaired or completely replaced.

The warm cell is used for low-activity chemical processing, pellet production, and final assembly. This cell is 13 ft wide, 56 ft long, and $16\frac{1}{2}$ ft high. A pair of manipulators is installed for each of nine windows and one manipulator for the tenth window. Other cell equipment includes a General Mills No. 100 mechanical arm and a 3-ton hoist.

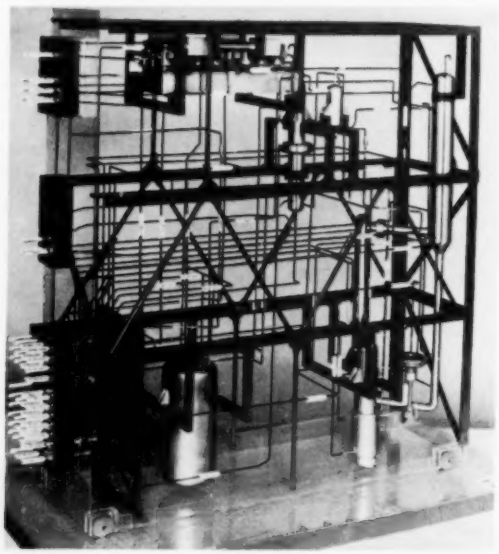


Fig. II-8 Model of solvent-extraction rack.[25] (Courtesy of Nuclear Power Division, Allis-Chalmers Mfg. Co.)

Operating equipment in the warm cell is fastened to base plates with locating pins and quick disconnects. The equipment is bagged and removed to the decontamination room when necessary. This equipment is maintained by direct contact after the activity has been reduced to acceptable levels.

Gaseous waste is scrubbed with caustic to remove ruthenium, iodine, oxides of nitrogen, and particulate matter. Liquid waste is stored in stainless-steel vessels at various activity levels. Very low-level waste is discharged to the environment.

Included in the report is a discussion of the economics and nuclear considerations involved in the PCUT facility. Some detail on equipment design is also given, although much of the design work will be done at the site. The authors express their belief that the PCUT program will be the clearest demonstration of the advantages of both the thorium fuel cycle and small-plant processing techniques.

The Kilorod facility at Oak Ridge National Laboratory (ORNL)[26] is also described in the Proceedings of the Thorium Fuel Cycle Symposium. The facility provides equipment for solvent extraction, preparation of U^{233}–thorium oxide by a sol-gel technique, loading the oxide in tubes by vibratory compaction, and closure and inspection of the loaded fuel tubes.

The solvent extraction (removal of U^{232} decay products) consists of feed preparation, one cycle of solvent extraction using 2.5% di-*sec*-butylphenyl phosphonate (D-*s*-BPP) in diethylbenzene as the extractant followed by product concentration. The uranium supplied to the facility will consist of uranyl nitrate solutions of varying concentrations and massive metal fragments. Dissolution of the fragments will be accomplished in a boiling mixture of 1.4*M* thorium nitrate solution containing 4 moles of free nitric acid per liter. A total mass of 4 kg of U^{233} metal will be charged to the batch dissolver vessel during one dissolution cycle. Criticality control in the geometrically unsafe tank will be assured by (1) the presence of thorium, which will give a U^{233}/thorium ratio of 0.025 and (2) maintaining the volume in the dissolver vessel such that the ever-safe concentration of U^{233} in light water may never be exceeded. The purification of the feed solution is accomplished in three pulse

columns in series. This is followed by boildown to 100 g/liter in a critically safe evaporator.

With the exception of the evaporator, the majority of the vessels are not of critically safe geometry; consequently, several important operational and equipment modifications have been made. The total mass of uranium within the facility will not exceed 5 ± 0.5 kg. Solutions will be maintained below the U^{233} ever-safe value of 10 g/liter by adjustments of flow rates for aqueous streams and chemical saturation of organic streams (except for the evaporator stream). In addition, pyrex glass rings (4% boron) have been placed in critical process vessels and enlarged column sections.

Oxide preparation and rod-fabrication steps are accomplished in shielded, alpha-tight cubicles installed in a 20-ft-long by 19-ft-wide by 27-ft-high processing cell. Operations will be accomplished by gloved hands or manipulator tongs.

Oxide particles are prepared by adding uranyl nitrate to a thoria sol in a slab type blend tank. A measured amount of this sol is added to a cascade tray dryer (Fig. II-9) consisting of eight shallow trays. The dried material is calcined in a standard resistance type furnace modified with a water jacket to prevent heating of the cubicle. After various grinding and classifying operations (Fig. II-10), a blend of the powder is compacted (vibration) into the rods which are then end-cap welded, decontaminated (ultrasonic cleaner), and helium-leak checked.

The Kilorod facility has been completed and operated[27] on cold and low-activity-level material (a thoria-urania fuel). Thorium and gross-gamma decontamination factors of 1100 to 2500 and 100 to 500, respectively, were measured. Sixty-five kilograms of specification-grade thoria–natural urania was prepared by the sol-gel technique during six shakedown runs.

A paper by Blanco and others[28] describes various equipment that might be applied to processing uranium-thorium metal or oxide fuels. Mechanical decladding[1] as tested on Sodium Reactor Experiment (SRE) fuel to be applied for the chop-leach method described in previous reviews[29] may be used. Core dissolution and extraction studies were made only on laboratory scale with small irradiated fuel pins or tracer levels.

Objectives of this program are to develop more economical processing methods and to derive from the data information to evaluate alter-

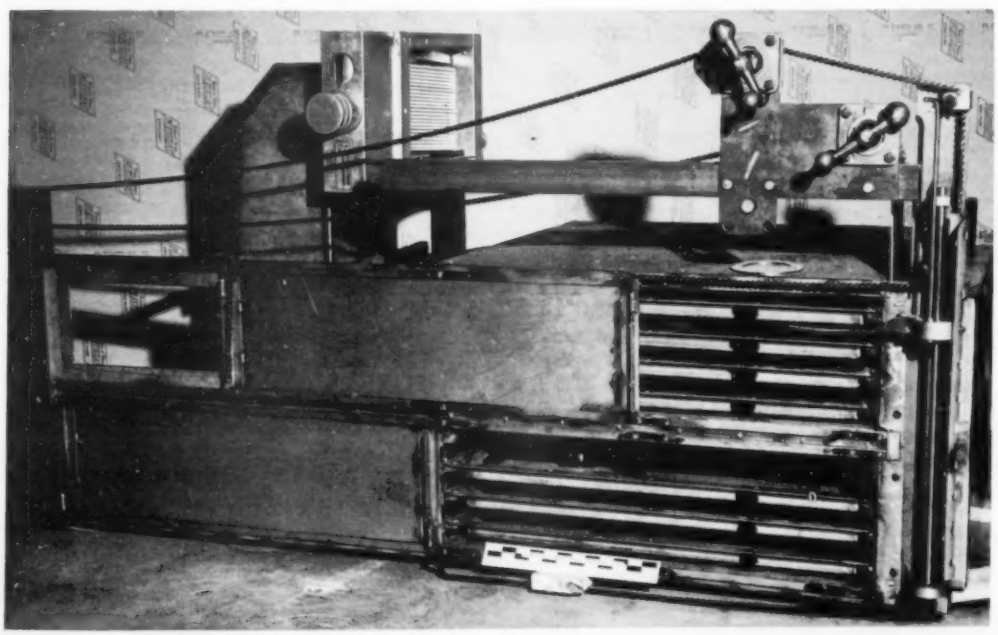


Fig. II-9 Tray dryer for the sol-gel process.[28]

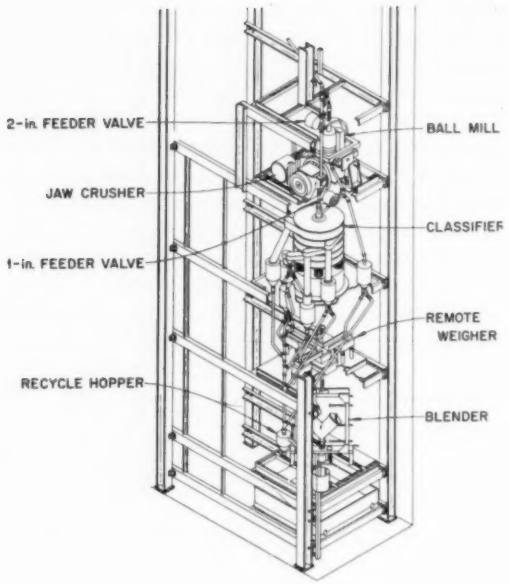


Fig. II-10 Powder preparation shaft.[26]

nate recycle systems. Major effort has been on stainless-steel-clad ThO_2-UO_2 fuels of the Consolidated Edison type, and graphite-bearing fuels similar to those proposed for the High-Temperature Graphite and Pebble-Bed Reactors. (D. M. Paige)

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Section

III

Reactor Fuel Processing

Research and Development on Nonaqueous Processing

Volatility Processes

Dry Halogenation Processes

Several processes that involve separation methods based on the relative volatility of chlorides are being developed for the processing of reactor fuel elements. Studies are currently being made on zirconium, molybdenum, and aluminum alloy fuels containing enriched uranium. Initial separation of uranium from the alloy is achieved by converting the alloying metal to a volatile chloride or oxychloride. Final recovery of uranium is achieved by fluorination to produce volatile uranium hexafluoride. Processes based on the fractional sublimation of chlorides are also being developed for ceramic fuels of low enrichment.

Uranium Alloy Fuels. Engineering-scale studies are continuing at Argonne National Laboratory (ANL) on a process for the recovery of highly enriched uranium from zirconium alloy fuels.[1] The process is based on the use of hydrogen chloride, at a temperature of 400°C, to convert the zirconium-uranium alloy to volatile zirconium tetrachloride and nonvolatile uranium trichloride. Recovery of uranium is achieved by the reaction between uranium trichloride and fluorine at 350 to 500°C to produce volatile uranium hexafluoride. Both reactions are conducted in a fluidized bed of inert alumina particles.

Process studies are being conducted in a nickel apparatus consisting of a $1\frac{1}{2}$-in.-diameter fluid-bed reactor and a $1\frac{1}{2}$-in.-diameter packed-bed filter. The packed-bed filter contains a bed of prefluorinated alumina particles and serves as a high-temperature filter for the retention of particulate solids entrained from the fluidized bed during the hydrochlorination reaction. Recent studies[1] have involved the successive hydrochlorination of several batches of alloy, followed by a single fluorination. In these studies, three equal-weight batches (total of 720 g) of 5 wt.% uranium–Zircaloy-2 alloy were processed. Data on the progress of the hydrochlorination reaction were obtained by continuous analysis of the off-gas stream with in-line thermal-conductivity cells. The data indicated that about 70% of the first batch of alloy had been reacted when the second batch was charged and that a total of 79% of the first two batches had been reacted when the final batch was charged. During the constant reaction-rate period, the alloy was reacted at a rate of about 70 g/hr, with peak rates of about 90 g/hr. The quantity of uranium lost through the packed-bed filter during the entire hydrochlorination period (20.5 hr) was about 0.1% of the total uranium charged. Data obtained from analyses of samples taken from the fluid bed during the fluorination period indicated that only 1 hr of fluorination at 350°C followed by 1 hr of fluorination at 500°C is required to achieve acceptable uranium concentration in the alumina beds. In this test the uranium retained by the alumina beds after fluorination was 0.5% of the total uranium charged. Data obtained during fluorination from the thermal-conductivity analysis indicated that about 90% of the uranium was recovered during the first 30 min of the low-temperature (350°C) fluorination period.

The volatile zirconium tetrachloride produced during hydrochlorination of zirconium-uranium alloy fuel represents a waste stream that requires processing for convenient storage. Zirconium tetrachloride is rapidly converted to solid zirconium dioxide by a gas-phase reaction with steam. Process studies are being made at ANL[1] to demonstrate this reaction in a 6-in.-diameter fluid-bed reactor. Satisfactory operation of the fluid-bed reactor has been achieved in tests employing zirconium tetrachloride feed

rates of from 4.1 to 5.1 kg/hr. Separate tests were performed with starting beds of sand containing a large fraction of fine particles (96.5% passing 100 mesh, 78% passing 200 mesh) which simulated the condition of extended-length operation wherein excessive amounts of fine particles would have accumulated in the beds. Satisfactory operation of the fluid-bed reactor was indicated by the following results of these tests:

1. No increase in pressure drop was observed across the sintered metal filters used to remove the fine particles from the exit gas stream.
2. Complete conversion of zirconium tetrachloride vapor to the solid oxide was obtained.
3. No caking or agglomeration of the bed material occurred.

Reilly and associates[2] and Williams[3] have published summaries of the work performed at Brookhaven National Laboratory (BNL) on the development of a process for the recovery of uranium from zirconium alloy reactor fuel elements. The process employed in this study involves the treatment of the zirconium alloy fuel with anhydrous HCl to remove the zirconium as volatile $ZrCl_4$. Uranium is recovered as volatile uranium hexafluoride in a subsequent fluorination step. Both steps of the process have been carried out in laboratory- and pilot-scale fluid-bed reactors. Descriptions of the process and equipment have appeared in previous issues of *Reactor Fuel Processing*.[4-6]

Faugeras[7] has described work in France concerning the processing of reactor fuels by volatility methods in fluid-bed reactors. These studies have concerned the development of process schemes for three types of alloy fuels: uranium-zirconium alloy clad with Zircaloy-2; uranium-aluminum alloy clad with aluminum; and uranium-molybdenum alloy containing 1.6% enriched uranium and clad with aluminum.

The principle of the method under development for recovery of uranium from zirconium alloy fuels is essentially identical to the process being studied at ANL.[1] Tests have been performed[7] in equipment capable of processing individual charges of 10 kg of alloy. The equipment includes a 20-cm-diameter fluid-bed reactor, a packed-bed filter, and a zirconium tetrachloride condenser. The fluid-bed reactor is charged with 3 kg of 20-mesh alumina, which serves as a support for the fluid bed, and 50 kg of 70-mesh alumina which serves as the fluid-bed material and in which the fuel charge is immersed. The packed-bed filter consists of two separate layers of alumina particles: 3 kg of 20-mesh alumina as a support for the filter medium and 14 kg of 70-mesh alumina particles (20 cm deep) as the filter.

The hydrochlorination reaction is carried out at 400°C with a hydrogen chloride feed rate of approximately 2 cfm. The fraction of the uranium entrained beyond the packed-bed filter is about 0.1%. Fluorination of the uranium trichloride solids is conducted at 300°C with a 10 vol.% F_2–90 vol.% N_2 gas mixture at a flow rate less than that required to fluidize the alumina particles. The bed is periodically fluidized to avoid continued channeling of the gas. Uranium hexafluoride is collected in a series of sodium fluoride absorption towers. The residual uranium content of the alumina bed is 200 ppm with respect to the weight of alumina and does not appear to increase with reuse of the bed material.

This method of processing nuclear fuels in fluid-bed reactors has been applied to uranium-aluminum alloy fuels clad with aluminum.[7] This alloy is treated under the same conditions as uranium-zirconium alloys. Volatile aluminum trichloride is produced by reaction of the alloy with hydrogen chloride at 400°C. Uranium is recovered as UF_6 by fluorination of uranium trichloride at temperatures between 300 and 600°C. Approximately 0.1% of the uranium is lost in the course of the hydrochlorination step. Workers at BNL[8] are also conducting studies on the processing of uranium-aluminum alloy fuels in a 1½-in.-diameter fluid-bed reactor.

Workers in the Department of Plutonium, CEA (France), have been investigating two alternative methods for processing molybdenum-uranium alloy fuels clad with aluminum.[7] Both methods utilize a decladding step wherein the aluminum is removed as volatile aluminum chloride by the action of hydrogen chloride at 400°C. The first alternative route incorporates a separate step in which the bulk of the molybdenum is volatilized as an oxyfluoride or oxychloride by the action of HF-O_2 or HCl-O_2 gas mixtures at a temperature of 500°C. Final recovery of uranium and plutonium is achieved by fluorination at 300°C. Complete details of laboratory-scale investigations of this particular route were reported in a previous issue of *Reactor Fuel Processing*.[9]

Since the elimination of molybdenum as either the volatile oxyfluoride or oxychloride is not complete (less than 90%), the step does not avoid the need for a subsequent separation of molybdenum from the hexafluorides after fluorination. Therefore the first route has been abandoned[7] in favor of a processing scheme that involves the direct fluorination of the alloy. Engineering-scale tests have demonstrated that the reaction between uranium-molybdenum alloy and fluorine can be conducted under controlled conditions in a fluid-bed reactor. Successful tests were performed using a reactant gas containing 45 vol.% fluorine in nitrogen and a bed temperature of 400°C. It is planned to separate the molybdenum hexafluoride from uranium hexafluoride by fractional distillation techniques.

Processes Based on Uranium Chlorides. A method for processing ceramic fuels of low enrichment based on the fractional sublimation of chlorides is being developed by Schmets and associates[10] at Centre d'Étude de l'Énergie Nucléaire (CEN) at Mol, Belgium. Uranium dioxide fuels are oxidized to U_3O_8 and then reduced to the dioxide to obtain a fine powder which is highly reactive toward chlorination. Uranium dioxide may be completely converted to volatile UCl_5 and UCl_6 by reaction with a gaseous mixture of chlorine and carbon tetrachloride. In order to obtain a pure UCl_4 product, it is necessary to add a reducing agent to the carbon tetrachloride. Good results have been obtained[10] by using a mixture of carbon tetrachloride and methane at 340°C.

In the processing of UC fuels, it is necessary to convert the fuel to UO_2 by oxidation prior to chlorination. Tests employing direct chlorination of UC by dry or moist hydrogen chloride have not given satisfactory results.

One aspect of this investigation has been to determine if various fission-product materials can be separated from uranium during chlorination of uranium dioxide. It was observed[10] that the niobium content of a Nb_2O_5-UO_2 mixture can be reduced to 12% of its original concentration, without producing a significant amount of volatile uranium chlorides, by reacting the mixed niobium and uranium oxides with a gaseous mixture of CCl_4 and water at 380 to 400°C.

A method for separating uranium from certain other elements that may be present in uranium dioxide fuels has been described by Ishihara and Hirano.[11] The method is based on volatilization of chlorides and selective condensation of uranium tetrachloride. In experiments that were conducted in a quartz reaction-tube assembly, CCl_4 vapor was flowed over irradiated UO_2. The volatile chlorides were selectively condensed in a series of condensers maintained at three temperature levels. Cerium was the main fission product which condensed with the uranium. It was observed that, by admixing natural CeO_2 with the uranium dioxide fuel prior to the chlorination step, the level of cerium activity in the uranium condensate would be decreased markedly.

Iwamoto and associates[12] have applied a chloride-volatility process to the processing of irradiated UO_2-graphite fuel elements. The major objective of the tests was to investigate the behavior of fission products during high-temperature chlorination with CCl_4. The possibility of employing a low-temperature (300°C) chlorination with chlorine gas was also studied.

Fluorination Process

A fluid-bed fluoride-volatility process is being developed at ANL[1] to recover uranium and plutonium from spent uranium oxide fuel elements that are clad with Zircaloy or stainless steel. The proposed process involves decladding by an appropriate reaction in a fluidized bed. Plutonium hexafluoride and uranium hexafluoride are formed upon reaction of the declad oxide fuel with fluorine. The hexafluorides may be separated from volatile fission products by distillation and from each other by thermal decomposition of plutonium hexafluoride.

Fluorination of Uranium Dioxide Pellets. At ANL[1] the fluorination of uranium dioxide pellet fuel is being studied on an engineering scale in a 3-in.-diameter air-cooled reactor with the aim of optimizing reaction rate, fluorine efficiency, and fluidization quality. In these studies, fluidization of inert, refractory alumina above the uranium dioxide pellets and in the voids of the pellet bed is used as an aid to heat removal. Current emphasis has been placed on the evaluation of a two-zone process wherein a mixture of oxygen and nitrogen is introduced into the lower reaction zone (oxidation zone), which is formed by the uranium dioxide pellet bed, and fluorine is introduced into the upper zone (fluorination zone), which consists of a

fluidized bed of alumina. Uranium oxide (U_3O_8) fines are formed in the lower zone and transported into the upper zone where they are converted to UF_6. In recent tests[1] it was shown that excessive rates of fines production and transport to the upper zone led to formation of intermediate uranium fluorides and plugging of the fluorine inlet port. Attention was directed toward establishing methods of reducing oxidation rates and improving fines transport from the oxidation zone. A method that incorporated gas-pulsing techniques has proved successful in avoiding difficulties associated with high rates of fines production. The gas pulsing was used with two 12-in.-deep fluidized-packed beds, 8.8 kg of UO_2, which were completely fluorinated using 4.5 and 6.0 vol.% oxygen in nitrogen in total processing times of 15 and 12.5 hr, respectively. Both the upper and lower zones of the reactor were maintained at 500°C. These processing times included a period of alumina bed cleanup using 100% fluorine and established the shortest processing times for 12-in.-deep beds of UO_2 pellets yet achieved in these fluorination studies. Sustained periods of high hexafluoride production rates were obtained in the runs; and a maximum rate of 107 lb of UF_6/(hr)(sq ft of reactor cross section) was demonstrated. Overall fluorine utilization efficiencies of about 70% were achieved in both runs.

Decladding of Stainless-Steel-Clad UO_2 Fuel. Two alternative methods are being investigated for decladding stainless-steel-clad UO_2 fuel elements: (1) the chemical destruction of the cladding by the high-temperature reaction with chlorine and (2) the removal of UO_2 pellets from the cladding by the oxidation of the pellets to produce U_3O_8 which forms as a very fine powder and readily separates from the cladding.

Workers at BNL[13] have investigated the decladding of stainless-steel-clad fuels by direct high-temperature chlorination. It has been observed that the reaction between stainless steel and chlorine gas becomes self-sustaining at a temperature of 675°C with a penetration rate of over 50 mils/hr. As reported in a previous issue of *Reactor Fuel Processing*,[14] under these temperature conditions the corrosion of nickel alloys in chlorine is sufficiently high to preclude their use as construction materials for this process. Therefore efforts at BNL[13] have been directed toward carrying out the chlorination reaction in a static bed of alumina particles wherein the walls of the reactor vessel are protected from the high heat of reaction by the insulating properties of the bed.

It has been observed at BNL[8,13] and at ANL[1,14] that uranium dioxide is readily attacked by chlorine gas under the proposed conditions of decladding. In recent work at ANL,[1] dry chlorine was reacted with a ½-in.-diameter ½-in.-long uranium dioxide pellet at 650°C for 3 hr, resulting in a 48% conversion of the uranium dioxide to uranyl chloride. Considerably less reaction (2% conversion) was observed in a test carried out at 600°C using an equimolar mixture of chlorine and nitrogen. Kangro[15] has studied the reactions of U_3O_8 and UO_2 with chlorine at temperatures between 1000 and 1100°C. The heat of the reaction for $U_3O_8 + 3Cl_2 = 3UO_2Cl_2 + O_2$ at 1050°C was calculated from equilibrium data to be +58.3 kcal/mole of U_3O_8. The heat of reaction for $UO_2 + Cl_2 = UO_2Cl_2$ at 1050°C was calculated to be +23 kcal/mole of UO_2.

Experimental work has been carried out at ANL[1] on the oxidation of uranium dioxide to U_3O_8 as a means of decladding chopped fuel elements in the fluoride-volatility process. Preliminary results on uranium dioxide pellets clad in type 304 stainless steel indicate that the oxidation scheme is feasible and that lower oxidation rates (air oxidation rather than oxidation in pure oxygen) result in greater removal of uranium dioxide as U_3O_8 from the cladding. Studies have also been undertaken[1] on the removal of UO_2 pellets from stainless-steel cladding by oxidation in a fluidized-packed bed. This process may then be incorporated into the two-zone oxidation-fluorination scheme for producing uranium hexafluoride. Preliminary tests have indicated that a high reaction temperature (500°C) and gas pulses improve the rate of separation of U_3O_8 from the cladding in a bed of 1⅛-in.-long fuel-element segments.

Properties of Fluorides

Uranium Fluorides. Settle and associates[16] at ANL have measured the enthalpy of formation of uranium hexafluoride by direct combination of the elements in a bomb calorimeter. This work is part of a continuing program at ANL to obtain thermochemical data by fluorine bomb calorimetry. Under appropriate conditions the reaction between metallic uranium and fluorine gas yielded a product of which approximately 99% was uranium hexafluoride

and only 1% was lower fluorides. A method for the quantitative determination of the lower fluorides was developed in order to make the required corrections. The derived data at 25°C are presented in Table III-1.

Table III-1 THERMOCHEMICAL DATA FOR URANIUM HEXAFLUORIDE[16] AT 25°C

	UF_6(c)	UF_6(g)
Energy of formation, $\Delta E_f°$, kcal/mole	−520.86 ± 0.43	−509.58 ± 0.45
Enthalpy of formation, $\Delta H_f°$, kcal/mole	−522.64 ± 0.43	−510.77 ± 0.45
Entropy of formation, $\Delta S_f°$, cal/(°)(mole)	−102.90	−67.01
Gibbs energy of formation, $\Delta G_f°$, kcal/mole	−491.96 ± 0.43	−490.79 ± 0.45

Fluorination of Uranium Compounds

Nikolaev and Shishkov[17] have studied the reaction between uranium tetrafluoride and chlorine trifluoride in the temperature range of 18 to 300°C. Uranium hexafluoride was formed in considerable yield (greater than 50%) in tests performed at temperatures as low as 18°C. It was observed that at temperatures below 100°C the nonvolatile residue contained the intermediate fluorides U_4F_{17} and U_2F_9; whereas at temperatures above 100°C, UF_5 was found, in addition to the previously mentioned intermediate fluorides, in amounts which increased with increasing temperature. In all tests the predominant gaseous reaction product was found to be chlorine; chlorine monofluoride was observed in insignificant amounts, and its occurrence was associated with side reactions. Nguyen-Nghi[18] has recently reported the results of a study on the kinetics of the reaction between uranium tetrafluoride and chlorine trifluoride in the temperature range of 25 to 50°C. In other work, Vandenbussche and Kikindai[19] have investigated the kinetics of the fluorination of UO_2, UF_4, U_3O_8, and UO_2F_2. Greene and Petit[20] at the Oak Ridge Gaseous Diffusion Plant have developed a method for the fluorination of uranium oxides to uranium hexafluoride using gaseous fluorine at a pressure of 1000 psi. The pressure is obtained by vaporization of liquid fluorine which has been condensed onto the uranium oxide and a potassium chloride activator contained in a metal reactor at liquid-nitrogen pressure. When the closed reactor is warmed within a safety shield, the fluorine vaporizes and the fluorination takes place very rapidly, usually before the reactor reaches room temperature. This fluorination procedure has had considerable success in preparing uranium hexafluoride specimens for isotopic analyses.

Chemical Reactions with the Hexafluorides of Uranium and Plutonium

Workers at ANL[1] have studied the reactions of uranium hexafluoride with hydrogen sulfide and carbon disulfide with particular emphasis on the determination and identification of the reaction products. In order to evaluate the difference in fluorinating behavior of UF_6 and PuF_6, the reaction between plutonium hexafluoride and carbon disulfide was also studied in detail.

Uranium hexafluoride vapor reacts readily with carbon disulfide vapor at room temperature. In the presence of excess carbon disulfide, the solid product is uranium tetrafluoride. When excess uranium hexafluoride is used, U_2F_9 is the solid product. When the reaction is carried out at 100 to 200°C with excess carbon disulfide, the gaseous products are sulfur tetrafluoride, sulfur hexafluoride, tetrafluoromethane, bistrifluoromethyl disulfide $[(CF_3)_2S_2]$, and possibly bistrifluoromethyl trisulfide. When the reaction with excess carbon disulfide proceeds to completion at room temperature, the main gaseous products are bistrifluoromethyl disulfide and bistrifluoromethyl trisulfide with traces of sulfur tetrafluoride. When the reactants are diluted with helium gas and the reaction is carried out at room temperature with excess carbon disulfide, the only organic gaseous product is bistrifluoromethyl disulfide.

Plutonium hexafluoride reacts vigorously with carbon disulfide at room temperature.[1] The solid product of the reaction is plutonium tetrafluoride. The gaseous products are sulfur tetrafluoride, sulfur hexafluoride, and tetrafluoromethane.

The reaction of uranium hexafluoride vapor and hydrogen sulfide vapor takes place readily at 25°C to produce uranium tetrafluoride, sulfur tetrafluoride, and hydrogen fluoride.[1] The reaction can probably be expressed by the equation

$$3UF_6(g) + H_2S(g) = 3UF_4 + SF_4 + 2HF(g)$$

In an experiment at 300°C (with a temperature excursion to 480°C), free sulfur was also

formed, probably through the disproportionation of sulfur tetrafluoride.

Properties of Uranium Fluorides

Benz and associates[21] at the Los Alamos Scientific Laboratory (LASL) have shown that the direct reaction of ammonium fluoride with uranium tetrafluoride or plutonium tetrafluoride yields a series of complex fluorides. Compounds which corresponded to the formula $NH_4F:MF_4$ (where M is either uranium or plutonium) were prepared in the mole ratios of 4:1, 2:1, 7:6, 1:1, and 1:3 by reaction of stoichiometric quantities in sealed tubes or by gravimetric arrests during NH_4F distillation. The corresponding U(IV) and Pu(IV) compounds were found to be isostructural.

Galkin and associates[22] have investigated the thermal decomposition of uranium ammonium pentafluoride (NH_4UF_5) and have observed that the decomposition occurs in two stages. In the temperature interval 320 to 360°C, a 5.9% loss in weight is observed; at 420 to 450°C, the loss in weight is 4.2%. At 360°C the decomposition of NH_4UF_5 is mainly due to the removal of ammonia. Above 450°C the product formed is uranium tetrafluoride. This suggests that a compound corresponding to HUF_5 is stable in the temperature range of 320 to 460°C.

Three complex cesium uranyl fluorides have been prepared and identified by Zaitseva and associates.[23] The compounds were isolated from aqueous solutions of uranyl fluoride and cesium fluoride. The chemical composition of the complex fluoride formed was found to depend strongly on the relative concentration of cesium and uranyl ions in solution. The compound $CsUO_2F_3$ exists when the ratio of Cs^{1+} to UO_2^{2+} is 0.5 to 1.5; at a ratio of 2 to 3, $Cs_2UO_2F_4 \cdot H_2O$ is formed; and at a ratio of 6 to 20, $Cs_3UO_2F_5$ is produced.

Rand and Kubaschewski[24] have published a book compiling and evaluating the thermochemical properties of uranium compounds. The authors not only cite over 200 references but also critically assess each reference on the accuracy of the data presented. In several instances the authors have recommended the use of thermodynamic data which they have determined in the course of their evaluation of the literature to be most accurate.

Properties of Plutonium Hexafluoride. The process of energy absorption by plutonium hexafluoride is of fundamental interest to the study of the decomposition of plutonium hexafluoride by radiation. Molar absorbencies of plutonium hexafluoride in the ultraviolet, visible, and near infrared spectral regions were determined at ANL.[1] The plutonium hexafluoride used in the study was prepared by fluorination of plutonium tetrafluoride with elemental fluorine at elevated temperatures. The plutonium hexafluoride was purified by trap-to-trap distillation under vacuum. The nickel cell used in this work was equipped with quartz windows and had a 5-cm light path. The location and molar absorbency index of the principal peaks are given in Table III-2. The absorption data indicate a rather complicated spectrum for

Table III-2 ABSORPTION SPECTRUM OF GASEOUS PLUTONIUM HEXAFLUORIDE, PRINCIPAL PEAKS[1]

[Cell Length, 5 cm; Window, Quartz; Temperature, 24°C; Instrument, Cary, Model 14; Pressures, Various (2.5 to 93 mm Hg)]

λ, Å	ν, cm^{-1}	Molar absorbency index, liters/(mole)(cm)
2,090	47,846	2,670
2,250	44,444	1,930
2,500 (broad)	40,000	1,300
3,155 (very broad)	31,695	760
4,142	24,143	15.2
4,260	23,474	13.4
4,376	22,852	14.1
4,480	22,321	12.0
4,550	21,978	9.3
4,600	21,739	8.0
4,750	21,053	6.4
5,420	18,450	3.2
5,610	17,825	6.5
5,840	17,123	3.9
7,500	13,333	1.4
7,870	12,706	7.76
7,960	12,563	5.41
8,165	12,247	7.08
8,265	12,099	5.97
8,390	11,919	5.25
8,500	11,764	3.50
9,360	10,684	6.29
9,735	10,272	2.82
9,870	10,132	3.42
10,075	9,925	27.3
10,245	9,761	8.96
10,435	9,583	12.0
10,700	9,346	0.83
15,600	6,410	0.60
20,900	4,785	0.80
21,100	4,739	1.59

PuF_6 with bands of sharp lines at 9583 to 10,684 cm^{-1}, two band groups at approximately 12,000 and 12,700 cm^{-1}, and several other bands before the very strong absorption in the 50,000- to 30,000-cm^{-1} region.

Plutonium hexafluoride decomposes by alpha radiation to plutonium tetrafluoride and fluorine. A kinetic study of the decomposition of PuF_6 by alpha radiation is being made at ANL.[1] The results indicate that the rate of decomposition is not a linear function of time. For tests in which the initial PuF_6 pressure was 50 mm Hg, the average decomposition rate for 12.6 days was 0.30 ± 0.04%/day; whereas for 157.7 days the decomposition rate decreased to 0.04 ± 0.01%/day. The data also show that, for nearly equal time periods, the rate of decomposition was slightly higher for an initial PuF_6 pressure of 100 mm Hg than for a PuF_6 pressure of 50 mm Hg.

The volatility of plutonium hexafluoride is utilized in fluoride-volatility processes to separate plutonium from most of the fission products. During the fluorination step and in subsequent operations, plutonium hexafluoride is exposed to radiation from fission products. A study of the decomposition of PuF_6 by gamma radiation has been undertaken at ANL[1] to obtain information concerning the extent of decomposition, the products of decomposition, and the fundamental processes involved in the radiation chemistry of PuF_6. Data obtained show an increase of the extent of decomposition with increasing amounts of energy absorbed in plutonium hexafluoride. Plutonium tetrafluoride and fluorine were identified as the products of the decomposition. The G value (number of molecules decomposed per 100 ev absorbed) for the PuF_6 decomposition is 7.5 ± 0.7. Experiments carried out on the decomposition of mixtures of helium and plutonium hexafluoride by gamma radiation have shown that helium has a slight effect on the decomposition of PuF_6, with the average G value being 6.0. Addition of krypton to PuF_6 reduces the extent of the decomposition by gamma radiation. A G value of approximately 3.8 is obtained for krypton pressures up to 1 atm and total energy absorption of less than 5×10^{21} ev. At a pressure of krypton greater than 1 atm or an energy absorption of 1×10^{22} ev, a G value of 1 is obtained. Addition of fluorine or oxygen to PuF_6 apparently reduces the extent of decomposition of PuF_6 by gamma radiation.

Preparation of Transition Metal Fluorides. Selig and Malm[25] at ANL have prepared pertechnetyl fluoride, TcO_3F, in gram quantities by the reaction of fluorine with TcO_2 at 150°C. Its properties are intermediate between those of permanganyl fluoride, MnO_3F, and perrhenyl fluoride, ReO_3F. Pertechnetyl fluoride is a yellow solid which melts at 18.3°C to a yellow liquid. The vapor pressure is represented by the following equations:

For the solid between −8.78°C and 18.28°C,

$$\log P = 12.448 - 3239.4/T$$

For the liquid between 18.28°C and 51.82°C,

$$\log P = 8.417 - 2064.6/T$$

The boiling point extrapolated from vapor-pressure measurements is about 100°C. Pertechnetyl fluoride is stable at room temperature.

Ruthenium tetrafluoride has been prepared recently by reducing with iodine ruthenium pentafluoride which was dissolved in pure iodine pentafluoride.[26] Ruthenium tetrafluoride is a nonvolatile, sandy-yellow compound which reacts violently with water, producing ruthenium dioxide. Ruthenium tetrafluoride may be handled in pyrex glass under dry conditions. Ruthenium tetrafluoride does not melt when heated to 280°C. Above 280°C it begins to react with glass.

When chromium powder is treated with elemental fluorine at 400°C and 200 atm in a nickel autoclave, both a bright-red chromium pentafluoride and a yellow, unstable chromium hexafluoride are formed.[27] The addition of small amounts of manganese to chromium powder and the use of a fluorine pressure of 350 atm at 400°C caused a significant increase in the yield of CrF_6. After the treatment was continued for 1 hr, the reaction product was transferred by vacuum to a trap which was cooled with liquid air and in which the CrF_6 was condensed. The excess fluorine in the trap was evacuated, and the yellow CrF_6 product that remained was observed to decompose rapidly at −100°C to give chromium pentafluoride and fluorine. (J. J. Barghusen)

Fused-Salt Volatility Process

Volatility processes are being developed to provide an alternative to conventional aqueous

processes for recovering uranium from spent nuclear fuels. The basic concept of all volatility techniques involves the conversion of uranium to a volatile compound such as uranium hexafluoride as the principal method of separating it from fission products. One such process, utilizing a fused-salt medium, is under development at Oak Ridge National Laboratory (ORNL).[28] The current primary interest at ORNL is the application to enriched uranium-zirconium alloy fuel. In the current ORNL zirconium-uranium process, fuel elements are dissolved in NaF-LiF-ZrF_4 (37.5-37.5-25.0 mole %) at 650 to 500°C, and the uranium is thereby converted to uranium tetrafluoride, which in turn is converted to volatile uranium hexafluoride with elemental fluorine at 500°C. A sorption-desorption cycle on a sodium fluoride absorber provides further decontamination of the uranium hexafluoride from volatile fission-product fluorides. Passage of the uranium hexafluoride through a bed of magnesium fluoride and collection of the uranium hexafluoride by cold trapping are the final steps in the process.

Several inherent advantages for the molten-salt fluoride-volatility process over conventional aqueous processes are claimed. These include the following:

1. Solid, highly concentrated waste is produced without further treatment.
2. Fewer process steps are required.
3. The process might be capable of handling certain refractory fuels (such as those containing BeO, ThO_2, and ZrO_2) which are not amenable to aqueous processes.

Modification of Pilot-Plant Equipment. The pilot plant was shut down 30 weeks for decontamination and modification of the equipment.

The pilot plant was modified (1) to improve product purity by the addition of a magnesium fluoride bed for technetium and neptunium removal, (2) to allow convenient recycle of off-specification product, (3) to provide a solids rod-out device in the hydrofluorinator off-gas line, and (4) to add the shielding needed for the higher radiation levels of shorter-cooled fuel. In addition, filters were installed to remove entrained sodium fluoride or other solid contaminants from product vapor. These filters use nickel wire-mesh packing and coarse nickel disks as filter elements. A nickel wire-mesh filter was also installed in the hydrofluorinator exhaust line to localize a radiation hazard by reducing the quantity of radioactive particles passing through a line to the ventilation-air scrubber. A settling chamber was installed in the waste salt off-gas vent line to reduce the amount of entrained solids.

Recent Flow-Sheet Runs with Fully Irradiated, Short-Cooled Fuel. After equipment decontamination and modification, five processing runs were completed in the fluoride-volatility pilot plant on zirconium-uranium alloy fuel. Three runs were performed to check plant equipment performance. Two runs were made to study fission-product behavior and uranium decontamination from fission products for 13-month-decayed and 6-month-decayed alloy, respectively. Burnup of this fuel was greater than 15%.

In the flow sheet used (Fig. III-1), the fuel elements were dissolved by HF at 680 to 500°C in molten equimolar NaF-LiF containing 25 to 45 mole % ZrF_4. During dissolution the zirconium-uranium alloy was converted to zirconium tetrafluoride and uranium tetrafluoride, both soluble in the fluoride salt. Submicron-size solids generated during the dissolution operation were scrubbed from the hydrofluorinator off-gas by liquid HF. After transfer of the salt mixture to a separate vessel, the UF_4 was converted to volatile UF_6 by fluorination at 500°C with elemental fluorine. The fluorination step separated the uranium from the bulk of the nonvolatile fission products. Further decontamination of the UF_6 from trace amounts of volatile and entrained fission products was accomplished by sorption on and desorption from a sodium fluoride bed at 100 and 400°C, respectively. While the UF_6 was sorbed on the bed, MoF_6 was desorbed by increasing the bed temperature to 150°C. Technetium and neptunium, which followed the UF_6 during desorption, were sorbed on the magnesium fluoride trap at 100°C and thereby removed from the UF_6. The product UF_6 from all runs was collected in cold traps.

A summary of conditions and results in the two runs with irradiated alloy are given in Tables III-3 and III-4.

Metallic cation impurities in the product are shown in Table III-5. The poorer removal of molybdenum and other impurities in run R-8 is attributed to HF dilution of the UF_6. The source of the HF is inleakage of moisture, which adsorbs on the NaF pellets and is sub-

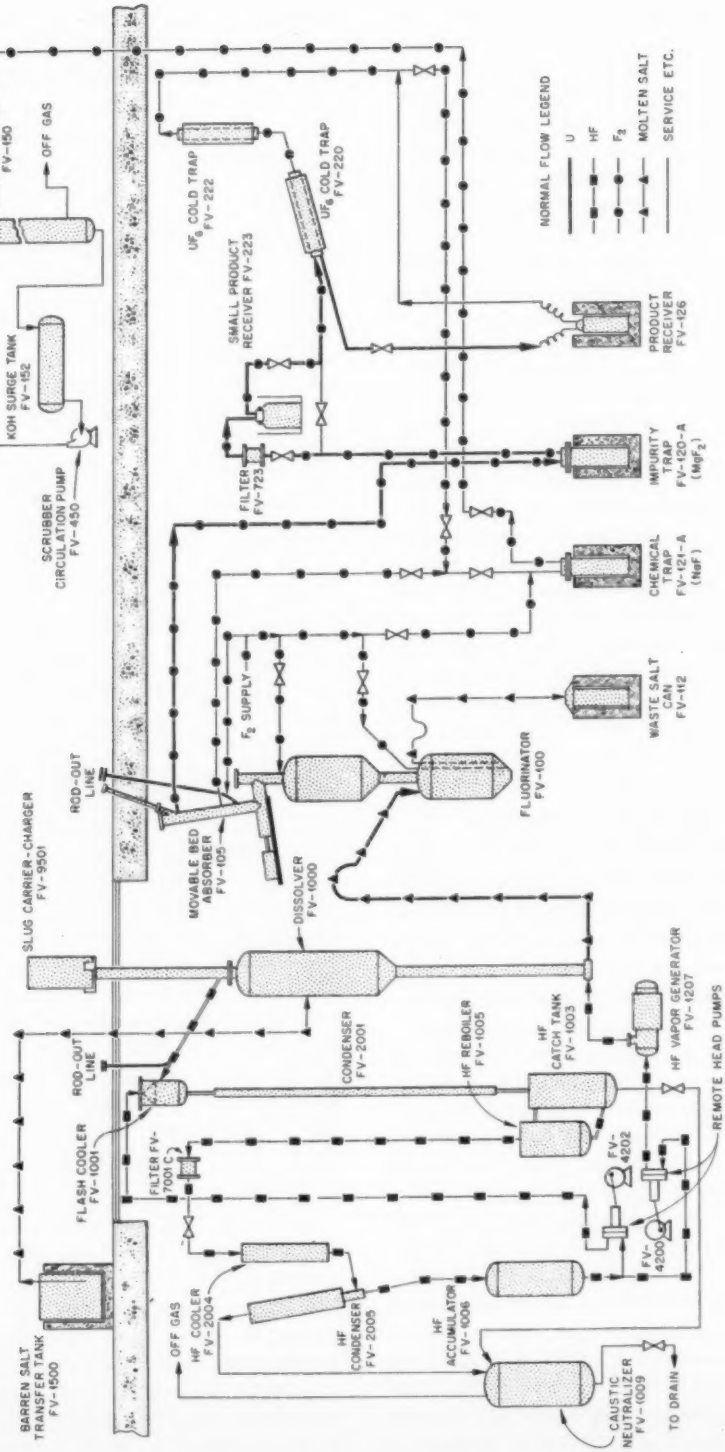

Fig. III-1 Schematic diagram of volatility pilot plant.[28]

Table III-3 SUMMARY OF DISSOLUTION RUNS IN THE VOLATILITY PILOT PLANT[28]

Run No.*	Salt temp., °C		Average dissolution rate,† kg/hr	Time,† hr	Average HF flow rate, g/min	Average HF utilization efficiency per pass through dissolver,† %
	Max.	Min.				
R-7	680	495	3.67	11.4	75–125	49.0
R-8	660	500	3.36	10.2	75–120	40.6

* Run R-7: enriched zirconium-uranium alloy fuel, decayed for about 13 months; ~40 kg of fuel; burnup greater than 15%. Run R-8: enriched zirconium-uranium alloy fuel, decayed for about 6 months; ~40 kg of fuel; burnup greater than 15%.

† Based on 90% completion of dissolution (complete dissolution would take about 30% longer).

Table III-4 SUMMARY OF FLUORINATION STUDIES IN THE VOLATILITY PILOT PLANT[28]

Run No.	Uranium concentration in salt, ppm		Fluorine flow, standard liters/min	Fluorination time, min	Fluorine utilization efficiency*	Fluorination time to obtain 10 ppm uranium in salt, min	Total nonrecoverable uranium losses	
	Initial	Final					g	wt.%
R-7	4485	4	6	101	13.7	105	0.9	0.09
			13	19				
R-8	4337	1	6	113	7.0	104	0.2	0.02
			13	30				

* Based on time required to obtain 10 ppm in waste salt (or final uranium concentration if greater than 10 ppm).

sequently fluorinated. Essentially complete decontamination of UF_6 product from fission-product activity was achieved; a summary of decontamination factors is given in Table III-6.

Modifications of the equipment are planned in order to reduce the moisture inleakage and to correct difficulties in the molten-salt sampler. In the current runs with irradiated alloy, additional shielding was required at certain points, such as valves, where unexpected deposition of radioactivity occurred. In general, the equipment performed without serious difficulty.

Corrosion Studies on the Fluorination Step. In the report[28] here reviewed, a summary is given of the metallographic analysis of corrosion test rods exposed in the L-nickel fluorinator of the pilot plant in earlier series of zirconium-uranium runs. These tests were discussed in a previous Review.[29]

Direct comparisons of alloys are not possible because of differing degrees of corrosivity of the various run groups, but the following alloys showed significantly better performance than L-nickel and thus are possible construction materials for a fluorination vessel: nickel filler metal 61 (INCO-61),* E-nickel,* Ni–5 Fe, Ni–1 Al, INOR-8,* and HyMu 80.* The total corrosive attack (metal loss and intergranular attack) measured for these specific alloy specimens in the molten salt (including the salt-vapor interface) ranged from 0.15 to 4.0 mils of fluorine exposure per hour. The scatter of data does not appear to permit selection of one superior alloy, however.

The Separation of Fission-Product Tellurium. Fission-product tellurium is important in the volatility processing of fuel cooled less than 200 days, especially since several volatile fluorides may be formed. In laboratory and pilot-plant tests, material balances on tellurium have been low, and this fact suggests that

* Alloy compositions (nominal percentages):

INCO-61	Ni, 93 min; Cu, 0.25; Mn, 0.60; Fe, 1.0; Si, 0.75; Al, 1.5 max.; Ti, 2-3.5
E-nickel	Ni; Mn, 2
INOR-8	Ni, 70; Fe, 5.1; Mn, 0.8; Mo, 16.5; Cr, 6.9; Si, 0.14
HyMu 80	Ni, 79.0; Mo, 20; Fe, 0.3; Mn, 0.5; Si, 0.5

Table III-5 CATION IMPURITIES IN THE URANIUM HEXAFLUORIDE PRODUCT FROM THE VOLATILITY PROCESS[28]

Run No.	Average product impurity level, ppm of U											
	Cr	Cu	Fe	Li	Mo	Na	Ni	Sn	Zr	Np	Tc	Total
R-7	<2	3	3	<1	9	129	15	<3	<1	4	<1	<171
R-8	<1	150	100	<1	43	327	30	<7	<1	48	4	<712
AEC specification*	<200			<10	<200							<300

* *Federal Register*, 25: 2817 (1960).

Table III-6 APPROXIMATE FISSION-PRODUCT DECONTAMINATION FACTORS FOR FUSED-SALT VOLATILITY PROCESS, 6-MONTH- AND 13-MONTH-DECAYED ALLOY[28]

Radionuclide	Uranium decontamination factor					
	13-month-decayed alloy (Run R-7)			6-month-decayed alloy (Run R-8)		
	For alloy dissolution* only	During volatile product recovery†	Overall process	For alloy dissolution* only	During volatile product recovery†	Overall process
TRE β‡		$>1\times10^{9}$			$\sim5\times10^{10}$	
Zr^{95}	50	$>1\times10^{8}$	$>5\times10^{9}$	10	1×10^{9}	1×10^{10}
Sr^{90}	2	$>5\times10^{8}$	$>1\times10^{9}$	2	$>1\times10^{9}$	$>2\times10^{9}$
Cs^{137}	3	$>1\times10^{9}$	$>3\times10^{9}$	1	$>5\times10^{9}$	$>5\times10^{9}$
I^{131}	10	$>5\times10^{4}$	$>5\times10^{5}$		$>1\times10^{6}$	
$Te^{(as\ 132)}$	300	$>1\times10^{5}$	$>3\times10^{7}$	5×10^{3}	$>3\times10^{8}$	$>1\times10^{9}$
Sb^{125}	250	$>1\times10^{5}$	$>2\times10^{7}$	5	$>1\times10^{8}$	$>5\times10^{8}$
Ru^{106}	750	$\sim1\times10^{5}$	$\sim1\times10^{8}$	1×10^{3}	$\sim1\times10^{5}$	$\sim1\times10^{8}$
Nb^{95}	100	$>1\times10^{7}$	$>1\times10^{9}$	50	1.6×10^{9}	8×10^{10}

* Based on ratio of calculated nuclide activity in alloy to measured activity in fluorinator.

† Based on ratio of measured nuclide activity in fluorinator to measured activity in product receiver. When product activity was below analytical limit of detection, the lower limit was used as the product activity for the decontamination factor calculation.

‡ Total rare-earth beta.

deposition on the nickel walls of the equipment had occurred. Recent laboratory attempts to prepare TeF_6 have shown tendencies for TeF_6 to be reduced by nickel metal at intermediate temperatures (up to 300°C).

The removal of TeF_6 from process gas streams containing fluorine is being studied by contacting with aqueous KOH. The results are to be used in evaluating the pilot-plant caustic spray scrubber used for removal of various toxic vapors from exhaust air before its release to the atmosphere. The gas mixture tested was about 12% TeF_6 in fluorine. The absorption system consisted of two heated columns (20 in. long and 1 in. in diameter) in series, packed with ¼-in. Alundum Berl saddles. A 10% aqueous KOH solution was circulated over the packing at a rate of about 205 ml/min. The countercurrent gas flow rate was about 100 ml/min. The TeF_6-F_2 mixtures were made by combining streams of metered flows. Approximate absorptions of 46, 68, and 67% of the tellurium, respectively, were achieved at 25, 50, and 70°C.

Fluorination Tests of Plutonium-Containing Fused Salt. The recovery of plutonium in the fused-salt volatility process is essential if the method is to be adapted to the processing of low-enrichment uranium fuels. In work with molten salts containing about 2 ppm plutonium, the volatilization of PuF_6 by fluorination was demonstrated along with recovery of the PuF_6 on fluoride salt beds. Additional work was carried out at higher concentrations, i.e., at about 1000 ppm plutonium in the salt. It was desired to determine whether the volatilization rate is significantly different at the higher plutonium concentration and whether the same sorption effects are observed with the larger

quantity of plutonium. Some preliminary work has been directed toward the examination of the rate-controlling step in the volatilization step, with the aim of finding process conditions for higher rates of volatilization.

Tests with LiF-NaF-ZrF_4 (31-24-45 mole %) mixture containing about 1000 ppm plutonium gave fluorination rates similar to those obtained at the concentration level of 2 ppm plutonium. The PuF_6 volatilization rate has a first-order dependence on the concentration, with the half time of the reaction being about 5.3 hr at 500°C and about 3.0 hr at 600°C. These results were obtained in 10-hr and 17-hr tests, respectively, at the two temperatures, with 55 g of salt in a 1-in.-diameter reactor with a fluorine flow rate of 100 ml/min at atmospheric pressure. In another test, preliminary results indicated that the reaction half time could be decreased to 1.5 hr by the use of fluorine at 40 psig (an acceptable rate for process use), provided that the pressurized fluorine does not markedly increase corrosion rates in the fluorinator.

A number of rate-controlling diffusion mechanisms can be postulated to account for the relatively low volatilization rates obtained with plutonium in fused salt. However, the results of two stirred-reactor experiments showed that the PuF_6 volatilization rate was not increased by violent agitation. Another hypothesis to account for the low rate is that the fluorinating agent (fluorine) has too low a solubility. A test run with intermittent additions of UF_4 was performed. It was thought that the fluorinating potential of the salt would be enhanced by the presence, at intervals, of the higher intermediate valent states of uranium. This run, however, had a half time of 4.0 hr, indicating that UF_4 addition had little effect. Although additional tests with agitation and using other fluorinating agents are planned, the best possibility of volatilizing PuF_6 without excessive corrosion (due to the long times required) is believed to be by salt-spray fluorination,[30] in order to minimize contact of molten salt with metal reactor walls.

In all the above fluorination tests conducted with about 1000 ppm plutonium in fused LiF-NaF-ZrF_4 (i.e., with about 55 mg of plutonium), material balances of 95 to 100% were obtained. This corresponds quite well with UF_6 behavior during volatilization from fused salts in laboratory work, and it indicates that a PuF_6-volatilization process would be feasible on an engineering scale if means can be found to limit corrosion to acceptably low amounts for the processing time required for complete plutonium recovery.

Sorption Tests on Plutonium Hexafluoride. An absorption process using CaF_2 or LiF may be feasible as a means of separating PuF_6 from UF_6. The volatilized PuF_6 in the above fused-salt tests was sorbed on various solid fluoride beds to examine sorption effects. In general, the absorption effects observed in the present work were similar to those found in tests at lower plutonium concentrations. Absorption beds of CaF_2, MgF_2, LiF, and NaF exhibited a definite selective trapping effect for PuF_6. A yellow color observed in tests made with CaF_2 and NaF indicated that complexes or compounds were formed.

The absorption results given in Table III-7 were used in calculating the 95 to 100% material balance in these plutonium volatilization experiments. The lithium fluoride used was prepared by fusing and fluorinating Li_2CO_3 and had a high specific surface area. The NaF (regenerated from $NaHF_2$), the CaF_2 (prepared by fluorinating $CaSO_4$), and the MgF_2 (prepared from slurried and dried powder) had surface areas, respectively, of 1.7, 14, and 60 m^2/g. Chemisorption appears quite probable in accounting for the quantity of PuF_6 sorbed on the materials of lower surface areas.

Hydrofluorination and Fluorination in a Single Vessel. The concepts of single-vessel dissolution by hydrofluorination followed by fluorination and of salt recycle are being evaluated on an engineering scale with process materials.

Table III-7 EFFECTS OBSERVED IN PLUTONIUM HEXAFLUORIDE ABSORPTION TESTS BY USING TWO CONSECUTIVE BEDS[28]

(8-g Beds of 12-20 or 20-40 Mesh Material in ½-In.-Diameter Tubes Held at 100°C)

Amount of Pu volatilized, mg	Bed 1		Bed 2	
	Material	Pu found, %	Material	Pu found, %
45.5	CaF_2*	91.4	NaF	8.6
9.7	MgF_2	97.7	NaF	0.3
28.8	LiF	>99†	NaF	0.01

* Yellow color observed, which is indicative of compound formation.

† Specific surface area of LiF was 42 m^2/g.

Dissolution experiments with Zircaloy-2 and zirconium-uranium alloy fuel elements indicate that salt recycle has no significant effect on rate and also show that filtration and/or settling steps for salt purification are not required. Corrosion rates measured during a series of single-vessel dissolutions and fluorinations were found to be not significantly different from the sum of the rates noted when the two process steps were carried out in separate vessels.

(W. J. Mecham)

Pyrometallurgical Processes

Pyrometallurgical processes for recovery of discharged reactor fuel materials include some processes in which metallic fuels are purified directly as metals and others in which metallic fuels and ceramic fuels are purified in liquid-metal–salt solvent systems. The potential economic advantages of these methods lie in their ability to handle short-cooled fuels, which makes possible minimum fuel inventories, and in the avoidance or simplification of chemical conversions.

The recent developments and current status of pyrometallurgical processes and of remote fuel fabrication for fast-reactor fuels were summarized by Lawroski[31] at a symposium on Fuel Cycles for Fast Reactors, held in Baden-Baden, Germany, in September 1963. He discussed in some detail the processes that will be tested in the Fuel-Cycle Facility adjacent to the Experimental Breeder Reactor No. 2 (EBR-II) at the National Reactor Testing Station (NRTS), Idaho, and presented estimates of fuel-cycle costs projected to the 1970's when it is expected that complete development and testing of a pyrometallurgical fuel cycle will have been achieved. The cost estimates for a plutonium-uranium alloy metallic fuel are given in Table III-8. The estimated total fuel-cycle costs range between 1.3 and 1.6 mills/kw(e)-hr, depending on the value placed on plutonium. The fuel-cycle costs for the metal fuel were stated to compare favorably with those of ceramic fuels which were assumed to be capable of threefold higher burnups than metallic fuels. Further, because fuel-cycle costs were less than those calculated using conventional solvent-extraction processes, Lawroski concluded that the competitiveness costwise of metallic fuels for use in fast reactors would be largely dependent on the successful application of pyrometallurgical processing and remote refabrication to such fuels.

Table III-8 ESTIMATED FUEL-CYCLE COSTS WITH ON-SITE PYROMETALLURGICAL PROCESSING AND REMOTE FUEL REFABRICATION[31]

(Metal Fuel with 3 At.% Burnup; 1000-Mw(e) Reactor and 80% Load Factor; Pu Price As Indicated)

	Mills/kw(e)-hr		
	$6/g Pu	$12/g Pu	$18/g Pu
Processing	0.42	0.42	0.42
Value of Pu loss (assumed at 1%)	0.04	0.08	0.12
Inventory (out-of-reactor fuel only)	0.09	0.18	0.27
Waste disposal	0.05	0.05	0.05
Replacement of alloying elements	0.10	0.10	0.10
Fuel fabrication	0.60	0.60	0.60
Total	1.30	1.43	1.56

Attention is directed to a recently published report, Research Highlights, of the Argonne National Laboratory's Chemical Engineering Division.[32] The development of pyrometallurgical processes is summarized, along with work in other program areas, through the year ending in May 1963. Inasmuch as the work in pyrometallurgical processing has already been reviewed in previous issues of *Reactor Fuel Processing* through other reports of the Division, no discussion of the Research Highlights report will be given here.

EBR-II Fuel-Cycle Facility

The EBR-II Fuel-Cycle Facility is a processing plant for recovery and purification of discharged EBR-II fuel material. A report has recently been issued[33] which gives a general description of the facility and of the operations to be conducted in it. As a single source of information, it is valuable in providing a general and useful picture of the fuel-cycle facility and its operations. Included for those who desire more information on a particular subject is a listing of published reports and articles on particular aspects of the facility.

Progress continues to be made in readying the EBR-II Fuel-Cycle Facility for processing discharged EBR-II fuel material[34–40] by mid-

1964. The facility includes a large (60,000 cu ft) argon-atmosphere cell in which processing and many of the refabrication operations are conducted. Operations not requiring the protection of an inert atmosphere are performed in an adjacent air-atmosphere cell. The Argon Cell was filled with argon in August 1963, and the argon purification system has been operated since that time to remove oxygen and water vapor from the argon.[34] With only day-shift operation of the purification system, the concentrations of impurities in the argon have been reduced to the following levels: 5.15% nitrogen, 45 ppm oxygen, and 45 ppm water.[34] The purification system does not provide for removal of nitrogen, whose concentration is permitted to range up to about 5% and is controlled at this level by intermittently purging a small fraction of the cell argon gas with high-purity argon. However, to provide for the contingency that nitrogen removal from the Argon Cell gas may be desired sometime in the future, a method is under development at ANL for removing nitrogen from argon by gettering the nitrogen with hot titanium sponge.[35] Two sets of experimental equipment are presently being constructed: (1) equipment for a study of the kinetics of nitrogen removal on hot titanium sponge and (2) a pilot plant for obtaining overall process performance data and information on component reliability.

Periodic determinations of the rate of air inleakage into the Argon Cell have been made. With an Argon Cell pressure of 2 in. H_2O below atmospheric, the air-inleakage rate was 0.005 scfm.[34] This is about half the estimated rate used in sizing the purification equipment.

Operations in the Argon and Air Cells are viewed through 31 shielding windows.[33] Each window is about 3 ft square and has a total thickness of 57 in. made up of six 9-in.-thick and three 1-in.-thick plates of glass (see Fig. III-2). Recently it has been shown that the innermost thick section of glass in a shielding window is susceptible to fracture during or after exposure to gamma radiation if the glass is chipped or stressed in some manner.[36] The discharge of the stored, gamma-ray-induced electrical charge results in a characteristic "tree-like" dendritic fracture observed in the electrical breakdown of other transparent insulating materials. Shown in Fig. III-3 are the internal fracture and the flash of light resulting from an electrical discharge in a 4-in. cube of lead silicate shielding glass exposed to 5.5×10^6 r of Co^{60} radiation.

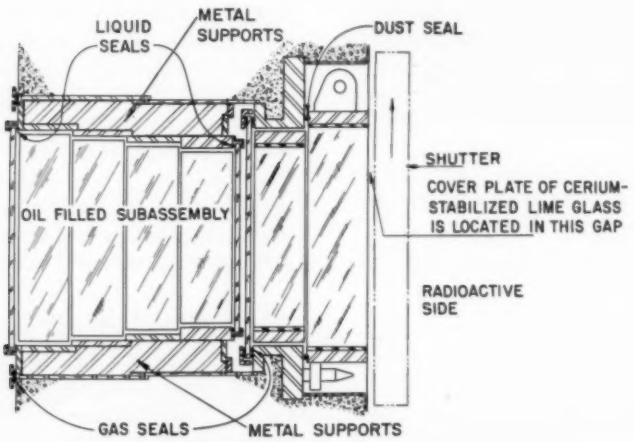

Fig. III-2 Shielding-window plan view.[33]

Because of the possibility that such an electrical discharge might be initiated by a bruising impact or by a stress concentration at a flaw, the shielding windows of the Argon and Air Cells are being protected from impact damage by mounting a $\frac{1}{4}$-in.-thick cover plate of cerium-stabilized lime glass on the innermost 9-in.-thick section of each window.[37] There will be an air gap of about $\frac{1}{8}$ in. between the cover plate and the inner plate of a shielding window.

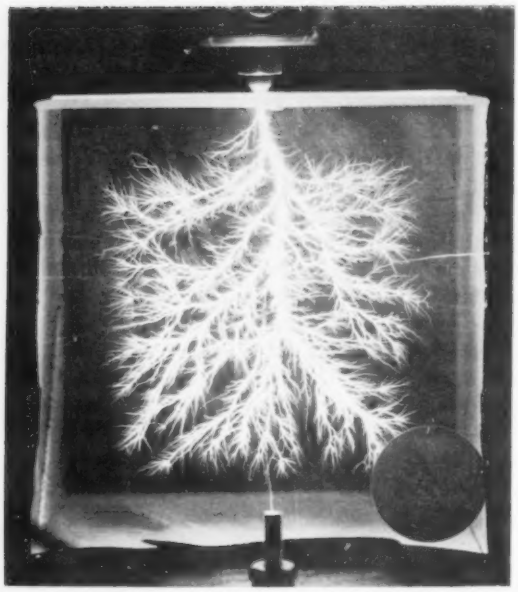

Fig. III-3 The light flash generated when a 4-in. cube of lead silicate shielding glass undergoes internal electric fracture is shown. The pointed probe at the top is dropped to trigger the electric breakdown. Exposure to Co^{60} was 5.5×10^6 r at 1.4×10^5 r/hr (Ref. 36).

Major items of equipment are being installed in the cell and operationally checked. Progress in equipment installation and cell corrective work is reviewed in recent progress reports of ANL's reactor development program.[34–40]

Melt-Refining Process Technology

Trice and Steunenberg have published the results of five small-scale melt-refining experiments with highly irradiated uranium-fissium alloys.*[41] These experiments were made to verify earlier data on fission-product removals obtained with unirradiated and low-activity alloys. In each experiment, about 400 g of uranium-fissium fuel pins, irradiated to between 0.22 and 1.75 at.% burnup, was melt refined for 1 or 3 hr at 1400°C in lime-stabilized zirconia crucibles. All experiments were conducted in the 140-liter bell-jar furnace shown in Figs. III-4 and III-5.

The behavior of fission products (see Table III-9) was consistent with earlier results.[41] Fission-product removals were over 99% for krypton, xenon, iodine, cerium, barium, and strontium; over 95% for yttrium, rare earths, and tellurium; and zero for all the noble-metal alloying constituents, except zirconium. A slight removal of zirconium (between 10 and 30%) is believed to have resulted from formation of zirconium carbide by reaction of zirconium with small amounts of carbon contamination present in the fuel alloy.

After the melt-refining operation, the product metal was poured into a mold. The yields were 15 to 30% lower than the yield expected in full-scale operation (10-kg charges). However, the yields obtained in these experiments were not regarded as meaningful because of the small scale of the tests and the unavoidable exposure of the fuel pins to air.

The irradiated pins were brittle and could be easily broken.[41] The swelling of the fuel pins, owing to the expansion of the contained fission-product gases, caused no difficulty in the melt-refining operation.

Purification of Metals by Various Melting Techniques

The purification of electrolytic grade uranium, melted and held in a UO_2 boat, by volatilization of impurities at 1250°C and by progressive solidification of the melt, has been reported by French workers.[42] Although less efficient than zone melting, the progressive solidification procedure (often called normal freezing) is faster and simpler. Clottes has reported some of the characteristics, e.g., electrical resistance, microhardness, and X-ray scattering, of uranium purified by zone melting[43] and has employed these measurements to calculate the recrystallization temperature of zone-melted uranium and to show that pronounced grain growth takes place during zone melting. The use of zone refining and electron-beam melting for the preparation of high-purity rare-earth metals has been discussed by Heinink.[44] Zone-melting calculation procedures, based on pure diffusional mass transfer, have been developed by Wilcox and Wilke[45] for approximating one-pass concentration profiles.

Eikenberry has reported on the refinement of small ingots of uranium by electron-beam

* The composition of the uranium-fissium alloy was approximately 2.7 wt.% molybdenum, 2.2 wt.% ruthenium, 0.3 wt.% rhodium, 0.2 wt.% palladium, 0.1 wt.% zirconium, 0.01 wt.% niobium, 10 wt.% U^{235}, with the balance being U^{238}

melting.[46] Concentrations of aluminum, chromium, magnesium, manganese, and lead were reduced by volatilization from the melt. Hydrogen and nitrogen were also removed from the uranium. Carbon was removed when zirconium was present in the melt, presumably through formation of zirconium carbide.

The purification of hafnium by electron-beam melting has been examined by Anable and Beall of the Bureau of Mines.[47] At low pressures and moderate energy inputs, most metallic impurities and hydrogen were removed in the first few minutes of operation; oxygen, carbon, and nitrogen were removed at slower rates. The mechanisms of purification and the effects of energy input rate and time were discussed.

The transactions of the 1962 Vacuum Metallurgy Conference include several papers related to the use of high-energy electron beams for welding and melting of metals.[48] Other topics covered in the field of vacuum metallurgy were casting, arc and induction melting, brazing, and degassing.

Hulsey has studied the effects of parameters involved in the design and performance of levitation melting coils.[49] Methods of achieving good heating efficiency are outlined. Other results of the study include a possible method for the measurement of surface tension of molten metals.

Development of Liquid-Metal and Salt Processes

Several processes are under development for the purification of reactor fuel materials in liquid-metal and salt systems. Purification of the fuel material is effected by selective extractions between immiscible metal and salt phases and by reactions within a single phase.

EBR-II Processes

At ANL, work was continued on the development of the skull reclamation and blanket processes of the EBR-II fuel cycle. Progress in the development of these processes is summarized in recent reports of the Laboratory.[34–40] The skull reclamation process provides for the recovery and purification of melt-refining crucible residues; the blanket process provides for the separation of plutonium bred into the EBR-II uranium blanket.

A modification of the skull reclamation process flow sheet has been made to allow the per-

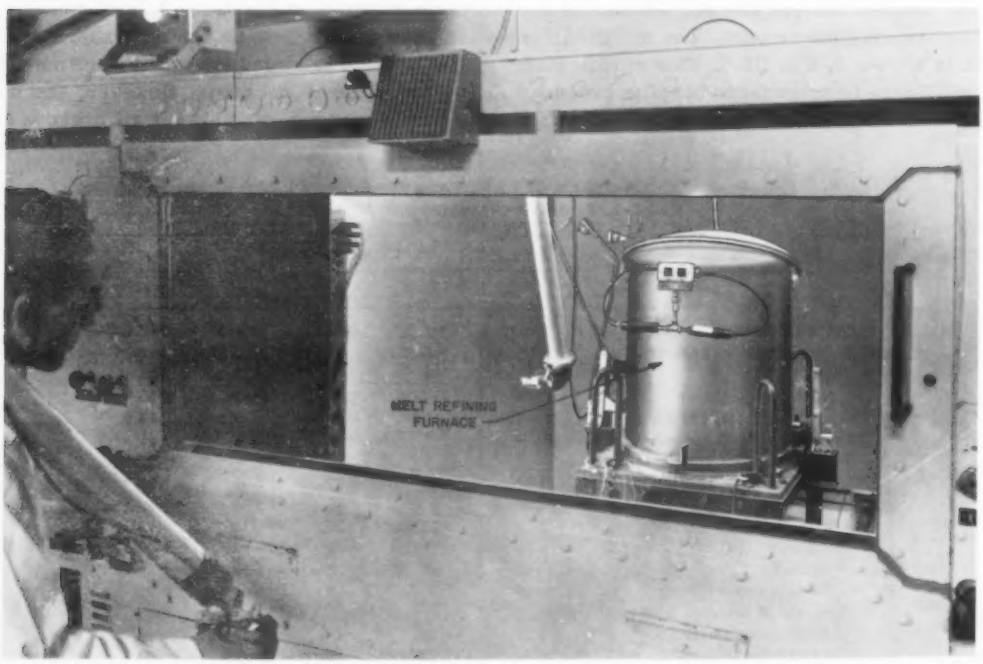

Fig. III-4 View of melt-refining furnace through cave window.[41]

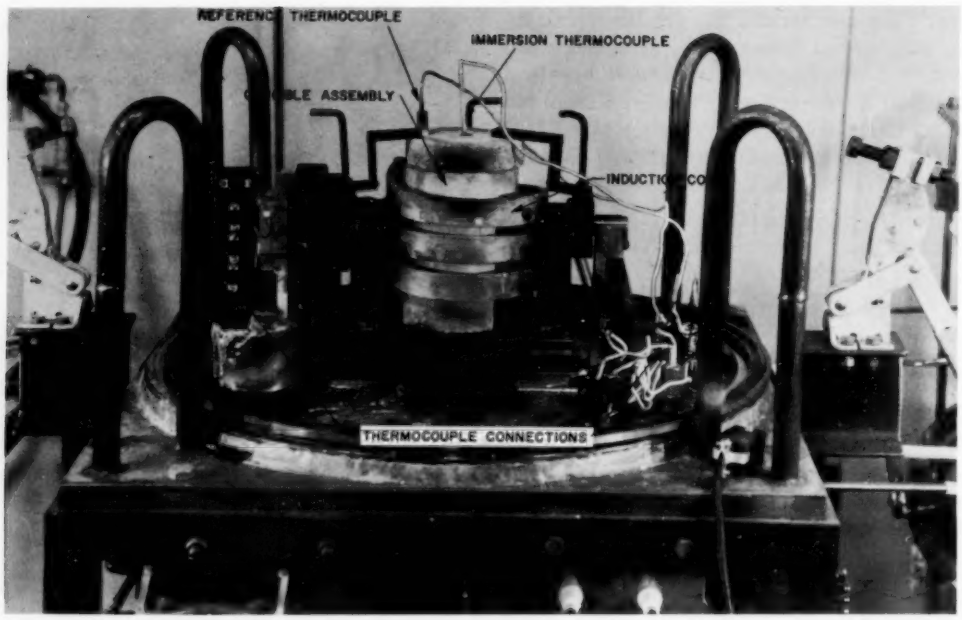

Fig. III-5 View of melt-refining furnace with the bell jar removed.[41]

formance, in a single tungsten crucible, of all process steps except the final step of evaporating the magnesium and zinc solvent metals and melting the uranium product. The modified flow sheet is shown in Fig. III-6. This modification was necessary because large beryllia crucibles which were to be used for the precipitation steps were wetted by the process solutions, thus making it impossible to remove the uranium product concentrate.[39] This behavior is in contradistinction to earlier experience with small beryllia crucibles which were not wetted by the process solutions. However, the use of a single tungsten crucible for all process steps

Table III-9 FISSION-PRODUCT REMOVALS IN HIGH-ACTIVITY-LEVEL MELT-REFINING EXPERIMENTS[41] AT 1400°C

	Experiment No.				
	1	2	3	4	5
Charge weight, g	387.6	392.3	362.5	364.2	382.2
Burnup, % of total atoms	0.56	0.22	0.74	0.87	1.75
Cooling, days	42	28	14	35	25
Total activity, curies	1170	1970	3800	3600	5350
Specific activity, curies/g	3.0	5.0	10.5	9.9	14.0
Duration of melt refining, hr	3	3	1	1	1
Fission-product removals, %					
Rare earths and yttrium	> 99	> 99	> 99	> 99	97
Tellurium	95	96	99	> 99	> 99
Zirconium	9	18	20	11	28
Iodine	> 99	*	> 99	> 99	> 99
Cesium	> 99	*	*	> 99	*
Barium and strontium	> 99	*	*	> 99	> 99
Removal of activity, % of total					
Total gamma activity	10	14	18	12	25
Total beta activity	82	81	84	83	84

* Datum not obtained.

except the final retorting step appears feasible and has certain advantages, the most important of which is the elimination of an entire furnace unit. The major disadvantage of a single crucible results from the necessity of dissolving the uranium product for transfer out of the crucible. This product solution, a 12% uranium–12% magnesium-zinc solution is less concentrated in uranium than the solid uranium concentrate (~60% uranium) obtained in a beryllia crucible, thus putting a greater load on the retorting operation. Fission-product removals and uranium losses are not affected by this flow-sheet change, which is more a modification of materials-handling procedures and equipment requirements than of chemical conditions.

Thorium Fuel Processes

At a symposium on the thorium fuel cycle, Chiotti presented a paper on the processing of thorium-uranium fuel by pyrometallurgical methods. The information contained in this paper has been presented in previous Reviews.[50–53]

A British patent has been issued to the Dow Chemical Company on the preparation of thorium-magnesium alloys by reduction of ThF_4 contained in a molten mixture of alkali and alkaline-earth fluorides with an excess of magnesium.[54]

Preparation of Metals by Reduction of Their Compounds

Closely related to and often involved in pyrometallurgical processes for purification of reactor fuels are procedures for the reduction of metal compounds. A substantial amount of information has been published on the electrowinning of metals from their compounds:

1. The electrowinning of uranium from uranium dioxide.[55] The electrolytic reduction of

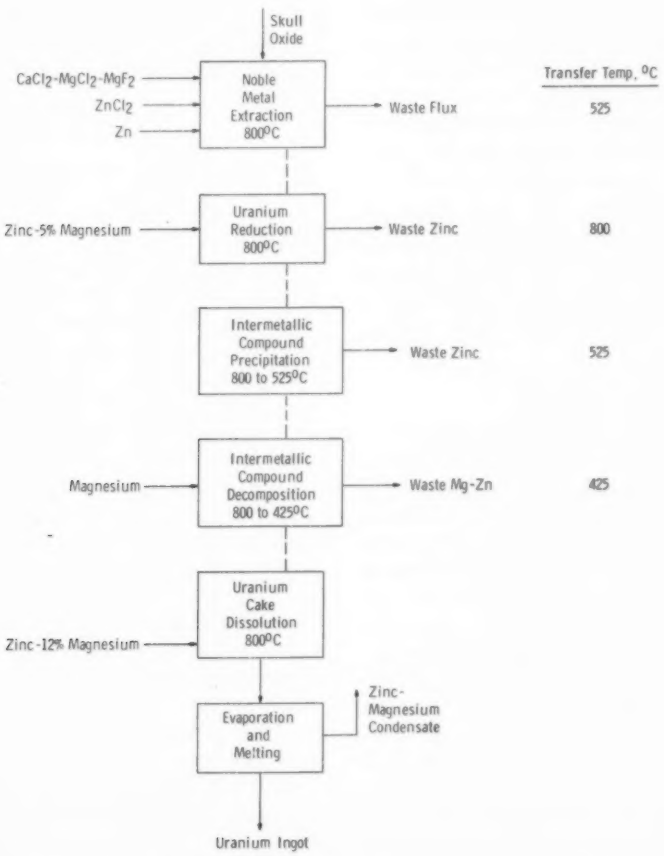

Fig. III-6 Flow sheet for skull reclamation process.[40]

UO_2 to molten uranium in fluoride baths operated at 1200°C has been demonstrated. Over 1000 g of metal with a purity of 99.8% was produced in some tests.

2. A patent issued to Slatin[56] on the production of alloys of titanium, zirconium, and hafnium by fusion electrolysis of their oxides or oxygen compounds.

3. A British patent issued to Euratom on an electrolytic process for preparation of pure metals, using a salt of the metal as an electrolyte.[57] A unique feature of this patent is the repeated application of mechanical pressure to the cathode deposit to inhibit the formation of a dendritic structure. The process can be used for all metals that are plastically deformable below the temperature of the salt melt and includes tantalum, thorium, plutonium, uranium, niobium, titanium, zirconium, hafnium, beryllium, and rare-earth elements.

4. A U. S. patent granted to Los Alamos workers on plutonium electrorefining cells.[58] The electrorefining process for production of high-purity plutonium metals has been discussed in a previous Review.[59]

5. A process for electrowinning cerium metal by electrolysis of molten $LiF-BaF_2-CeF_3$ systems with either CeO_2 or CeF_3 as the feed.[60]

The reduction of U_3O_8 by an exothermic aluminum-U_3O_8 reaction has been investigated by Fleming and Johnson.[61] The results suggest the possibility of a novel fuel-fabrication process and could also affect reactor safety evaluations.

Fundamental Studies Relative to Liquid-Metal Process Development

Considerable fundamental information is being accumulated on the chemistry of liquid-metal and salt systems and is essential to the successful design of pyrometallurgical methods of processing reactor fuels.

Solubility Studies

The zinc-calcium system has been investigated as an alternative to the zinc-magnesium system as a solvent system in which to process uranium-plutonium fuel alloys. Solubility data for uranium and plutonium in zinc-calcium solutions are shown in Figs. III-7 and III-8. Comparison of these figures shows plutonium solubilities to be much higher (by factors of 10^3 to 10^4) than the corresponding uranium solubilities in zinc-calcium solutions having high calcium concentrations. However, in the region of 39 to 68 wt.% calcium and at temperatures of 528 to 729°C, the presence of uranium decreases plutonium solubility by factors of about 1.5 to 3.5. The phase diagram of the calcium-zinc system has been reexamined by Messing, Adams, and Steunenberg,[62] and several alterations in the diagram were shown to be necessary.

Solubility studies of plutonium in cadmium have shown a peritectic transformation at 404°C with solubilities above and below the peritectic temperature being represented by:[39]

$$\log (\text{at.\% Pu}) = 5.7916 - 4040.6\ T^{-1}\ (°\text{K}) \quad (330 \text{ to } 404°\text{C})$$

$$\log (\text{at.\% Pu}) = 3.2293 - 2304.8\ T^{-1}\ (°\text{K}) \quad (404 \text{ to } 505°\text{C})$$

This peritectic transformation temperature was confirmed by galvanic cell studies[36,39] which placed the transformation temperature at 403°C.

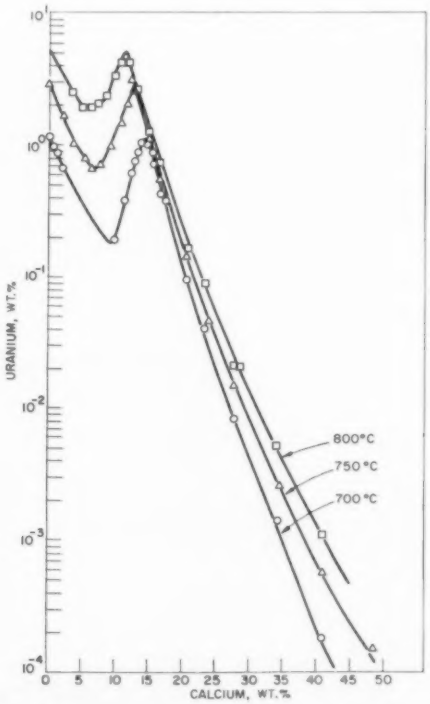

Fig. III-7 Solubility of uranium in zinc-calcium solutions.[37]

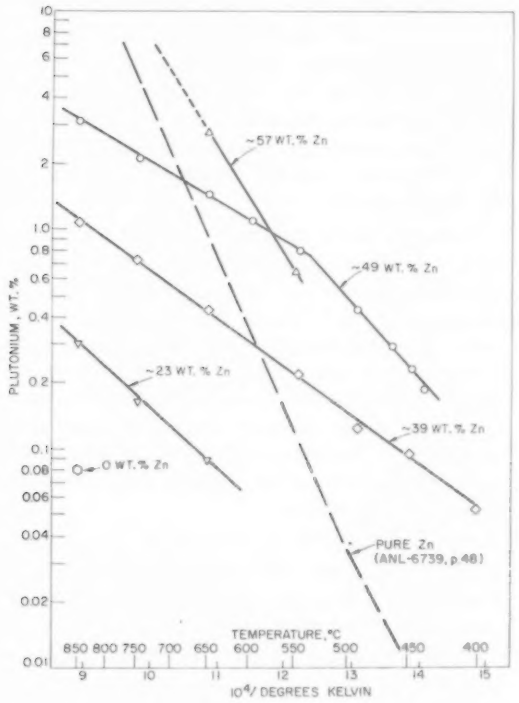

Fig. III-8 Solubility of plutonium in zinc-calcium solutions.[37]

One of the solid phases in the plutonium-cadmium system has been identified[37] as $PuCd_{11}$ (cubic, isotypic with $CeCd_{11}$). Another phase having a pattern similar to rare-earth compounds of the MCd_6 type has been revealed by X-ray analysis, which also showed the presence of at least one other compound. A number of other phases, in addition to the MCd_6 type, have been tentatively identified[37] in the europium-cadmium, gadolinium-cadmium, and ytterbium-cadmium system by Knudsen effusion cell measurements.

The solubility of rhenium in zinc has been tentatively placed at less than 0.04 wt.% at 750°C (Ref. 36). This compares with solubilities of 25 and 0.11 wt.% at 750°C for manganese and technetium, indicating decreasing solubility with increasing atomic weight for these elements which are in the same group in the periodic table. In the technetium-zinc system, the most technetium-rich intermetallic phase has been identified by effusion measurements as Tc_2Zn_{11} (Ref. 40).

The solubility of various metals (aluminum, silver, uranium, thorium, copper, manganese, nickel, antimony, titanium, cobalt, and chromium) in mercury have been determined by Jangg and Palman.[63] Solubilities were determined by analyses of filtered saturated amalgams. Peritectic breaks were observed in some systems. The heat of solution was about equal for all metals, and, on this basis, Jangg and Palman critically reviewed values of the solubility of iron reported in the literature. Solubilities of chromium, titanium, zirconium, tantalum, and columbium in mercury have been reported by Weeks and Fink[64] (see subsection on Construction Materials for Liquid-Metal Systems where the solubilities are discussed in connection with mercury corrosion studies).

Distribution of Elements Between Metal and Salt Phases

The Japanese have studied the distribution of a large number of elements between liquid bismuth and a liquid LiCl-KCl eutectic salt[65] at 550°C. Equilibrium was approached from both the metal and salt phase and was studied as a function of time up to four days. Distribution coefficients (K = weight concentration in salt/weight concentration in metal) are as follows: Mn, 10^5; Fe, > 20; Co, > 300; Cu, 7; Ag, 0.05; Zn, > 2000; and Cd, > 1500. Selected distribution values obtained when equilibrium was approached from only one of the phases are: Mg, > 400; Sr, > 870; Sc, > 190; La, > 10^5; Gd, > 2000; Cr, > 2000; Mo, > 12,700; W, > 18,000; Tc, < 0.08; Pt, < 0.003; In, > 9; Sn, < 0.6; Sb, < 0.003; Te, < 0.05. The K for polonium was 0.1 after 5 hr of contacting.

Viscosities of Liquid Metals

Considerable information relative to the viscosities of liquid metals has become available. Grosse has developed an empirical relation between the activation energy of viscous flow and the melting point of a metal,[66] from which the viscosity of a metal at any temperature may be calculated by Andrade's equation as follows:

Grosse's relation:

$$H_\eta = 0.431\ T_M^{1.348}\ (T_M \text{ between 200 and 2000°K})$$

Andrade's equation:

$$\eta\ (\text{viscosity}) = a \exp\ (H_\eta / RT)$$

By these relations, Grosse found satisfactory agreement between calculated and experimen-

tally determined values of the viscosity of liquid plutonium.[67]

Physical properties for metals of reactor interest are being determined at Mound Laboratory. The viscosities, densities, and self-diffusion coefficients of lanthanum, cerium, and praseodymium from their melting points to 1000°C have recently been reported.[68,69] Viscosity determinations are being made on a series of plutonium-iron alloys.[70] Because the period of oscillation of the oscillating cup viscosimeter which is being employed is very sensitive to the presence of a solid precipitate, it was shown that the liquidus temperature of an alloy could be determined from the intersection of lines drawn through viscosity data points obtained above and below the liquidus temperature.[70]

Ofte and Wittenberg of the Mound Laboratory have published data on the viscosities of bismuth, lead, and zinc from their melting points[71] to 1000°C.

Bismuth: $\log \eta = 0.3368\ (1000/T) - 0.3510$
Lead: $\log \eta = 0.4506\ (1000/T) - 0.3338$
Zinc: $\log \eta = 0.6625\ (1000/T) - 3841$

where η is in centipoises and T is in degrees Kelvin.

Construction Materials for Liquid-Metal Systems

Work through October 1962 on the containment of liquid-metal fuels has been reviewed by Thamer.[72] Among the systems discussed are the plutonium-iron and plutonium-cerium-cobalt alloys for the Los Alamos LAMPRE reactor, uranium-based alloys (U-Cr, U-Mn, and U-Fe), and bismuth solutions of uranium. Some observations were also made on corrosion by liquid-metal coolants.

Materials for Plutonium Systems

One of the major objectives of the LAMPRE-I reactor (Los Alamos Molten-Plutonium Reactor Experiment) is the evaluation of combinations of plutonium fuel alloys and container materials in a reactor environment. At the present time the reactor is being operated with a plutonium–10 at.% iron alloy contained in tantalum-base capsules. Table III-10 gives the results of metallographic examination of five of nine tantalum fuel capsules which were removed from the LAMPRE reactor.[73] With the exception of capsule 1268 which had undergone low reactor exposure, all had been intergranularly penetrated by the fuel alloy in the heat-affected zone just below the closure welds. This suggests that a major problem exists in developing a satisfactory welding technology for sealing the fuel capsules.

Platelets were regularly observed in the irradiated capsules near the external surface of the weld which had been in contact with the sodium coolant.[73] These had not been observed with any regularity in out-of-reactor tests. Formed on a set of orthogonal planes (see Fig. III-9), the platelets isolated large blocks of tantalum, some of which were dislodged from the surface. They are believed to be compounds, e.g., oxides, formed by reaction with impurities in the sodium coolant.

Gross leakage of fuel (~ 30 g) had occurred from capsule 1454. The gas pressure of 200 psi (corrected to reactor operating conditions) was only about one-third that calculated from the reactor exposure. At the fuel-vapor interface, the wall of this capsule had thinned from the inside of the capsule to about 60% of the original thickness. This wall thinning was observed in three of the nine capsules.

Out-of-pile loop testing of tantalum containers continues to show the superiority of double arc-melted tantalum to electron-beam-melted tantalum for containment of the plutonium-iron alloy.[73] However, butt welds of double arc-melted tantalum also are intergranularly penetrated by the plutonium-iron alloy. Apparently, changes in the metallurgical or chemical properties of the tantalum in the weld area are the cause of the intergranular penetration by plutonium fuels.

Further tests are being made of the compatibility of plutonium-cobalt-cerium alloys with tantalum.[73] Under some conditions, a Ta_6Co_7 cobalt reaction layer forms on the tantalum and spalls off into the fuel. No reaction layer was formed on either carburized or uncarburized tantalum specimens tested simultaneously in a cobalt-cerium alloy. The carburized layer on the specimen partially dissolved in the melt and coated the bare tantalum specimen with a uniform carbide layer. Because this suggests that carburized layers may be self-heating, tantalum capsules with carburized layers are being tested with the plutonium-iron alloy fuel.

Table III-10 METALLOGRAPHIC EXAMINATIONS OF TANTALUM FUEL CAPSULES REMOVED FROM LAMPRE-I REACTOR[73]

(Capsules Contained a Plutonium–10 At.% Iron Alloy)

	Capsule No.				
	1268	1393	1260	1251	1454
Mwd (reactor)	2.3	64.7	104.5	104.5	104.5
Container	Ta–0.1 W	Ta–0.7 W–0.2 Y	Ta–0.1 W	Ta–0.1 W	Electron-beam-melted Ta
Platelets (weld)	No	No	Yes	Yes	Examination incomplete
Precipitates (body of cap)	Yes	No	No	Yes	Examination incomplete
Intergranular precipitation (at fuel weld)	No	Severe	Slight (~0.0002 in.)	Severe	Examination incomplete
Soln. attack (anywhere)	No	No	No	No	Yes
Comments	Short reactor exposure	One of few capsules without platelets	No apparent damage	Large sections of Ta lost due to platelets intersecting in weld	Fuel (~30 g Pu) leaked out of capsule

Bowersox of Los Alamos has measured the solubility of tantalum in high-purity plutonium over the temperature range[74] of 700 to 1000°C. The solubility of tantalum increased from 45 ppm at 700°C to 1070 ppm at 1000°C and may be represented by the following equation:

$$\log (\text{mole fraction Ta}) = 3.06 - 750 \times 10^{-3}\, T^{-1}\ (^{\circ}\text{K})$$

In survey experiments, the solubility of tantalum in the 10 at.% iron-plutonium alloy was found to be about double that in the high-purity plutonium.[74]

Materials for Uranium Systems

Extensive corrosion of tungsten by molten uranium at 1200°C and by a uranium-chromium eutectic alloy at 900°C has been reported.[40] Tantalum was also severely corroded by uranium at 1200°C. Neither tantalum nor tungsten would be suitable containers for molten uranium.

Materials for Mercury Systems

The long-term corrosion resistance of various carbon steels and refractory metals to liquid mercury and mercury vapor at temperatures between 600 and 1400°F is under study at BNL because of the potential application of mercury as a turbine-driving fluid in reactor power plants. Titanium and zirconium have been employed in the mercury as corrosive inhibitors (through formation of protective films), and magnesium has been used for wetting and deoxidation purposes. In capsule tests, protective TiN and ZrN films were observed on carbon-steel specimens, but none were found on Haynes 25 alloy specimens.[64] The materials under study have been fabricated into natural-circulation boiling loops (see results for carbon and Croloy steels in the Fall 1963 issue of *Reactor Fuel Processing*[64]). A columbium–1% zirconium alloy loop failed after 7700 hr of operation when cracks developed in the superheater section of the loop. Continuing in operation are a pure tantalum loop (2670 hr) and a zirconium-pretreated carbon-steel loop (3560 hr). Severe boiling instabilities, believed to be associated with corrosion (and therefore intimate wetting) in the condensing section, have been encountered with the latter loop. To test the hypothesis that corrosion in the condensing section leads to boiling instabilities, a loop fabricated of an 18-8 stainless steel, which is known to be rapidly attacked by boiling mercury, has been placed in operation. Construction has also begun on a forced-circulation, boiling mercury loop which is being fabricated of the columbium–1% zirconium alloy.

The solubilities in mercury of some of the additives and materials under test have now been measured.[64] The solubilities of columbium

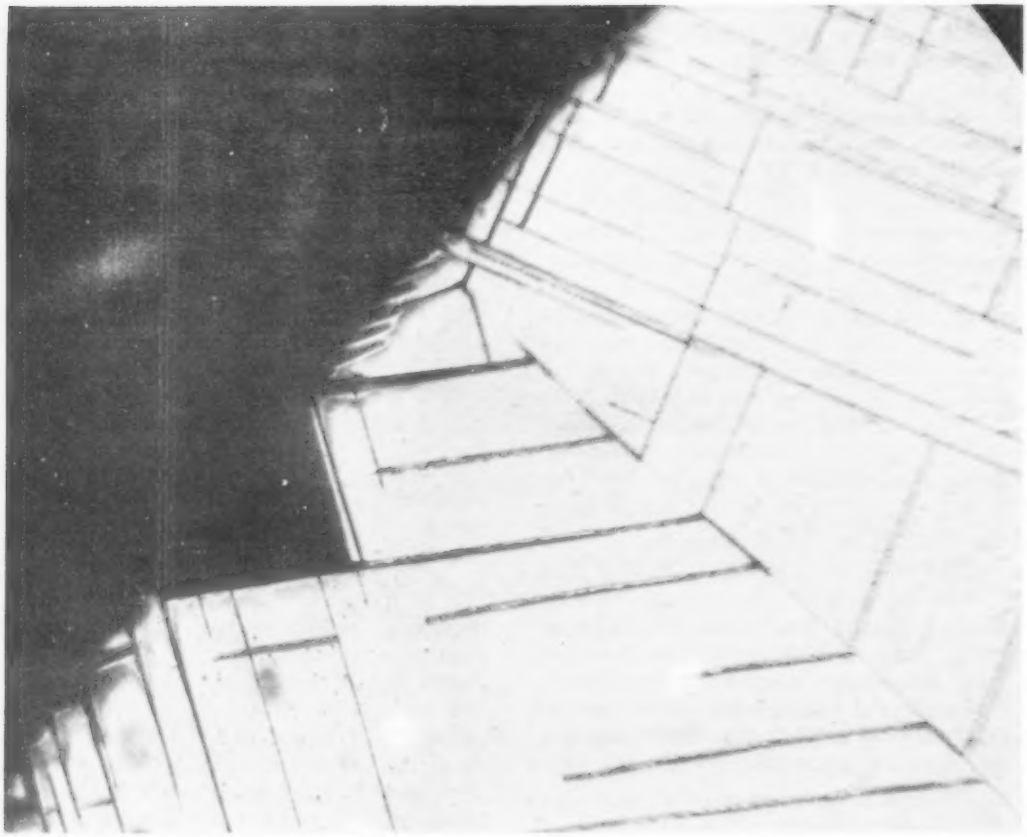

Fig. III-9 Platelets in weld area of tantalum capsule.[73] Capsule No. 1251 (see Table III-10); observed under polarized light. [Magnification, 300 × (before reduction)].

and tantalum were too low to be measured. The solubility of zirconium decreased from about 1000 ppm at 720°C to about 20 ppm at 560°C, of titanium from about 100 ppm at 640°C to about 5 ppm at 500°C, and that of chromium from about 30 ppm at 650°C to about 1 ppm at 540°C.

Materials for Alkali-Metal Systems

The corrosion resistance of refractory metals to sodium and its vapor in the temperature range of 1400 to 2400°F is also under investigation at Brookhaven.[64] Less than ½-mil corrosion was found in columbium–1% zirconium boiling sodium reflux capsules after 5000 hr of operation. A high-velocity boiling sodium loop fabricated of the columbium–1% zirconium alloy is under construction and another is being designed.

At ANL, special columbium alloys are being tested in a search for improved fuel cladding materials for sodium-cooled reactors. A sample of columbium–5% molybdenum showed no loss in room temperature ductility after a 500-hr exposure at 650°C to flowing sodium containing 1 to 5 ppm of Na_2O (Ref. 39). In contrast to this, a columbium–4.33% zirconium sample was completely embrittled. Columbium-base alloys exposed to sodium having an abnormally high oxygen content (200 ppm) showed wide variations in behavior.[36]

The MSA Research Corp. is investigating the effects of sodium on austenitic and ferritic steels[75] at 1200°F. Two loop facilities are in operation for studying fatigue, creep-rupture, creep rate, and tensile properties of 2¼ wt.% chromium–1 wt.% molybdenum steel and type 316 stainless steel in air, helium, and sodium.

Some tests are being made with sodium containing high oxygen and carbon contents.

Interpretation of corrosion by sodium depends to a large extent on knowledge of the oxygen and carbon contents. Improved analytical methods for oxygen are being sought at Argonne and BNL. At Brookhaven, an isotopic dilution technique involving O^{18} has been selected.[64] At Argonne, an activation method that depends on the $O^{16}(p,p)N^{16}$ reaction is being explored.[40] Kirtchik and Riechmann have also reported on analytical methods for oxygen in sodium.[76] Steinmetz has described equipment used for analyses of oxygen and carbon in sodium[77] and has also discussed the development of a continuous oxygen meter,[78] based on an electrochemical method, for monitoring the oxygen content of sodium.

General Publications in Liquid-Metals Field

Two additional issues of bulletins which review and abstract current literature in the liquid-metals field have been published: (1) the twenty-second in a series on liquid-metals technology by the MSA Research Corp.[79] and (2) the third in a series of high-temperature liquid-metal technology reports by BNL.[80] Epstein has published two reports[81,82] giving his general observations and impressions of liquid-metal studies in Great Britain and France. One[81] gives particular attention to the names of British and French workers and to describing ideas and techniques which might be of interest to the U. S. program. (L. Burris)

Other Nonaqueous Processes

Pyrochemical processes, which are being developed mainly for oxide and carbide reactor fuels, generally employ gases, molten salts, and liquid metals as reagents and process media. Pyrochemical and pyrometallurgical techniques are similar in the use of dry, high-temperature reactions, a capability for handling short-cooled fuels, and the use of simple, compact equipment. The distinguishing feature of pyrometallurgical processes is that the major fuel constituents remain in the metallic state throughout the process, whereas in pyrochemical processes chemical conversion steps are utilized. By aqueous solvent-extraction standards, both types of processes provide low fission-product decontamination, and they are therefore best suited for closed, remotely operated fuel cycles.

Oxide Fuel Processing

Development work has continued at Hanford on the salt-cycle process, a closed-cycle electrolytic procedure for the recovery of uranium dioxide–plutonium dioxide fuel of the type proposed for the Plutonium Recycle Test Reactor (PRTR).[83–85] This process involves mechanical decladding, gaseous oxidation of the fuel to form a mixture of U_3O_8 and plutonium dioxide, and dissolution of the oxide mixture in a molten chloride bath, e.g., equimolal LiCl-KCl, by sparging with chlorine or hydrogen chloride. In this process the major portion of the uranyl chloride in the salt solution is first reduced electrolytically with a graphite cathode; essentially plutonium-free uranium dioxide, which is a by-product of the process, is deposited. The uranium and plutonium remaining in the salt solution are then codeposited electrolytically on a graphite cathode as a mixture of the dioxides. This deposit is sufficiently enriched in plutonium so that it can be recycled to the reactor core. This process has been reviewed in a recent report[86] in which the electrodeposition aspect is emphasized.

The current goal of the salt-cycle process is to recover over 99% of the plutonium with no more than 5% of the uranium.[84] In recent studies, up to 94% of the plutonium has been codeposited with about 10% of the uranium from a LiCl-KCl melt (mole ratio 1 : 1) containing 20 wt.% uranium and 0.2 wt.% plutonium. From a melt containing only 0.02 wt.% plutonium, codeposition under similar conditions resulted in the recovery of 90% of the plutonium with 15% of the uranium. In both cases the final plutonium concentration in the melt was approximately 0.002 wt.%. In another experiment, a high plutonium recovery of 99.8% was demonstrated. However, this high value was achieved at the expense of an accompanying high uranium recovery of 72%. In other experiments, with a platinum cathode, plutonium enrichment factors as high as 44 were achieved, and mixed oxide deposits containing up to 36% plutonium dioxide were obtained.[85] Substitution of LiCl-CsCl eutectic (58 mole % LiCl) for equimolal LiCl-KCl solvent resulted in a higher decontamination

factor for promethium, a representative rare-earth fission product. However, it also increased the extent of plutonium dioxide codeposition with uranium dioxide by-product (in the first step) to the extent that it is doubtful that an adequate plutonium-uranium separation would be possible.

As an alternative to the codeposition step of the salt-cycle process, the plutonium in the molten-salt solution can be precipitated selectively as plutonium dioxide by sparging the solution with an oxygen-chlorine mixture. The uranium is then recovered by electrodeposition of uranium dioxide on a graphite cathode. Further studies have been reported on this process.[84] Cerium was used as a stand-in for plutonium in a 20-liter salt bath containing LiCl-KCl (mole ratio 2.5:1). Among several devices used to contact the circulating oxygen-chlorine sparge gas with the melt, the best recovery of cerium dioxide (65%) was obtained with a bed of quartz chips.

Engineering studies on the salt-cycle process have included the production of 410 lb of uranium dioxide by electrolysis in an equimolal LiCl-KCl bath.[85] The size distribution of the product was as follows:

Size fraction	Wt.%
−4 +10 mesh	36
−10 +35 mesh	37
−35 +65 mesh	12
−65 mesh	15

The lithium content of the water-washed product was 15 to 30 ppm, and the chloride content was 100 to 200 ppm for all of the size fractions. About 300 lb of the material had an oxygen-to-uranium ratio averaging 2.005. For the remainder of the material, which was produced from melts containing some moisture, this ratio varied from 2.007 for the −4 + 10 mesh fraction to 2.040 for the −65 mesh material. The carbon content of the product was 20 to 30 ppm when pyrolytic graphite electrodes were used and 150 to 200 ppm when nuclear grade graphite electrodes were employed.

Reactions of Plutonium and Uranium Species in Molten Chloride Media

Spectrophotometric studies of the behavior of plutonyl species in molten chloride solvents have continued.[83] In melts sparged with an oxygen-chlorine mixture, the ratio of plutonyl(VI) to plutonyl(V) was found to decrease with rising temperature; at constant temperature the ratio was found to be proportional to the square root of the chlorine concentration in the sparge gas. This behavior is consistent with the equilibrium reaction

$$PuO_2Cl_2 \rightleftharpoons PuO_2Cl + \tfrac{1}{2}Cl_2 \qquad (1)$$

At certain temperatures and chlorine concentrations, a precipitate is formed, probably via the reaction

$$PuO_2Cl \rightleftharpoons PuO_2 + \tfrac{1}{2}Cl_2 \qquad (2)$$

This latter reaction appears to proceed toward completion with increasing temperature and to proceed in the reverse direction with increasing chlorine concentration in the sparge gas.

The composition of the solvent has been found to have a strong influence on the relative amounts of different plutonium species under these conditions. The ratios of plutonyl(VI) to plutonyl(V) and of Pu(IV) to Pu(III) were both greater by a factor of 3.5 in LiCl-CsCl (mole ratio 1.4:1) than in equimolal LiCl-KCl at 550°C. The solubilities of chlorine in these melts are being determined in an effort to obtain meaningful equilibrium constants for these plutonium oxidation-reduction reactions.

There is an interesting parallel between the behavior of plutonium and that of uranium in molten chloride melts. The reactions of plutonium species reported above may be compared with results obtained on uranium at Hanford[87] and at Argonne.[87] It was reported previously that the higher oxides of uranium react with magnesium chloride-based melts to form uranyl(VI) chloride, which decomposes at high temperature (~ 650°C) and low chlorine pressure to uranyl(V) chloride and chlorine

$$UO_2Cl_2 \rightleftharpoons UO_2Cl + \tfrac{1}{2}Cl_2 \qquad (3)$$

Further studies of this reaction have been made in LiCl-KCl eutectic (59 mole % LiCl), in NaCl-KCl-$MgCl_2$ eutectic (30, 20, and 50 mole %, respectively), and in equimolal LiCl-$MgCl_2$ (Ref. 88). Increasing temperature and decreasing chlorine pressure were found to drive reaction 3 in the forward direction. Through a combination of spectrophotometric data and chlorine pressure measurements, an

equilibrium constant of 10^{-6} atm was found for the reaction in LiCl-KCl eutectic at 650°C. The equilibrium was somewhat dependent on the composition of the solvent. At temperatures above about 700°C, precipitation of uranium dioxide began to occur,[89] presumably via the reaction

$$UO_2Cl \rightleftharpoons UO_2 + \tfrac{1}{2}Cl_2 \qquad (4)$$

Gaseous Low-Decontamination Process for Uranium Dioxide

Additional results have been reported by Atomics International[90-92] on the gaseous oxidation-reduction (AIROX) process for uranium dioxide reactor fuels. The fuel cycle, which utilizes remotely operated equipment, entails pulverization of the refractory uranium dioxide fuel pellets by alternate oxidation with air or dilute oxygen at 200 to 600°C, and reduction with hydrogen at 600°C. The powdered uranium dioxide product is reenriched by blending and is then refabricated by cold pressing and sintering.

It was reported previously[93] that uranium dioxide fuel pellets can be removed from stainless-steel cladding by puncturing the cladding and then converting the pellets to a powder by the gaseous oxidation technique. Additional studies have been made in which uranium dioxide clad with thick-walled stainless steel (wall thickness, 0.035 in.) was successfully declad. Both low-density and high-density fuels appear to be amenable to this treatment. In one case in which the oxidized material became tightly wedged in the cladding, one reduction-oxidation cycle removed 95% of the fuel.

Methanol vapor has been found to be an effective reagent for the reduction of uranosic oxide to uranium dioxide.[91] It has the advantage that lower-temperature operation is possible (350 to 400°C, instead of about 600°C). Two cycles of methanol reduction and air oxidation gave a loosely sintered product with a very fine particle size.

The enhancement of uranium dioxide reactivity toward hydrofluorination is discussed in Sec. V of this issue.

In its present form the AIROX process is not designed for fission-product removal, although a few fission products such as the rare gases and cesium appear to be released in the various process steps. A possible modification of the process whereby those fission products with high neutron-capture cross sections may be largely removed has been investigated at Atomics International.[94] In Table III-11 is shown the relative extent of neutron capture by fission products (exclusive of the rare gases, cesium, and Sm^{149}) calculated to be present in irradiated uranium dioxide fuel. No neutron-capture data are listed for rare gases, which are assumed to be released during the oxidation-reduction cycle, for cesium, because it is removed in the sintering step, or for Sm^{149}, because it reaches an equilibrium concentration in the reactor. Excluding these fission products, the elements listed in Table III-11 account for about 95% of the total neutron capture. Neodymium and samarium account for about 40%. These latter two elements were selected as being typical of rare-earth fission products.

On the basis of thermodynamic data (which indicate the formation of rare-earth chlorides to be more favorable at lower temperatures) together with vapor-pressure information, two procedures were investigated: (1) Uranium dioxide powder was treated with hydrogen chloride below 1000°K to form chlorides of the fission-product elements; then the material was heated under vacuum to 1500°K to volatilize the chlorides. (2) Chlorides of the fission products were formed as in procedure 1 but were later vaporized by heating the powder to a temperature above 1500°K in hydrogen chloride to which hydrogen had been added to suppress the formation of volatile uranium chlorides. Either mixed or individual fission-product oxides were added to the uranium dioxide charges.

Table III-11 RELATIVE NEUTRON CAPTURE OF FISSION-PRODUCT ELEMENTS[94]

(Basis: UO_2 in a Boiling-Water Reactor After One Burnup Cycle of 15,000 Mwd/Metric Ton. Values Do Not Include the Effects of Inert Gases, Cesium, and Sm^{149})

Element	Neutron-capture contribution, %
Neodymium	25.0
Rhodium	16.1
Samarium	14.5
Technetium	12.2
Promethium	11.1
Europium	10.8
Molybdenum	3.3
Praseodymium	1.5
Lanthanum	1.0
Others	4.5
Total	100.0

It was found that blended powders of the rare-earth oxides and uranium dioxide did not simulate adequately the behavior of spent fuel material. Fission-product removal was more difficult from material that had been prepared by coprecipitation or irradiation.

The results obtained with the latter materials indicated that by treating the uranium dioxide powder with a gaseous mixture of hydrogen and hydrogen chloride for 5 hr at 1650°K neutron capture resulting from the fission-product elements in spent fuel (Table III-11) should be decreased by about 50%. An additional treatment with chlorine gas for 3 hr at 750°K appears to remove over 90% of the molybdenum and ruthenium, corresponding to an additional 3% of the neutron capture. Rhodium, which accounts for 16% of the neutron capture, was not removed by either of these treatments. It was suggested that future work include a study of technetium behavior and that an attempt be made to improve the removal of rare-earth elements by using a fluid bed in order to eliminate bed thickness effects.

As a continuation of a recycle demonstration, pellets that were refabricated from processed uranium dioxide fuel which had been irradiated to burnups of 5700 to 15,000 Mwd/metric ton have been placed in the Materials Testing Reactor (MTR) for further irradiation.[92]

Carbide Fuel Processing

At Atomics International, investigations have continued on three processes for the recovery of uranium carbide reactor fuels.[90–92] In the first process the carbide is oxidized by oxygen, air, or carbon dioxide at temperatures of about 400 to 500°C; then the resulting oxide is reconverted to uranium monocarbide by carbothermic reduction at or above 1300°C. The second process involves nitridation of the fuel by nitrogen at about 900°C to form a mixture of uranium sesquinitride and carbon. This mixture is then reconverted to uranium monocarbide by heating in vacuum above 1500°C. In the third process (the electrolytic process),[95] the uranium carbide fuel is dissolved anodically in a LiCl-KCl bath, depositing metallic uranium on a molybdenum cathode. Liquid-metal cathodes are also being considered as an alternative. The cathode deposit is dissolved in mercury, and uranium monocarbide is formed by distillation of the mercury in a hydrocarbon atmosphere. Only the electrolytic process provides significant fission-product decontamination; the other two are essentially refabrication procedures that permit reenrichment of the fuel and the repair of irradiation damage.

Processing by the Carbide-Oxide-Carbide Cycle

Previous studies had shown that, whereas freshly arc-melted uranium monocarbide is relatively unreactive toward oxygen and nitrogen, the reactivity increases markedly upon several days exposure of the material to moist air. To investigate the role of surface area in this phenomenon, uranium monocarbide samples of varying surface area were exposed to either 200 mm of oxygen or 400 mm of nitrogen at 850°C (Ref. 90). The results, listed in Table III-12, indicated that the oxidation and nitridation rates tended to increase and the ignition temperature in oxygen tended to decrease with increasing surface area of the carbide. The oxidation behavior of the first two samples was similar to that observed previously for partially "activated" carbide, and the behavior of the third sample was characteristic of the "reactive" carbide. It is suspected that atmospheric hydrolysis of uranium monocarbide results in a greater surface area and correspondingly increased reactivity.

Table III-12 OXIDATION AND NITRIDATION RATES OF URANIUM MONOCARBIDE OF VARYING SURFACE AREA[90]

(Conditions: 200 mm Oxygen at 850°C; 400 mm Nitrogen at 850°C)

Surface area, cm^2/g	Oxidation results		Nitridation results
	Weight gain, mg/(min)(g)	Ignition temp., °C	Weight gain, mg/(hr)(g)
9.5	1.93	415	7.8
31.3	4.46	415	6.0
135.0	7.74	300	136.5

Oxidation studies have been conducted with uranium monocarbide containing fission-product elements to simulate recycled fuel.[91,92] The samples were prepared by carbothermic reduction of uranium dioxide containing 2.5, 5.0, and 7.5% fissia,* followed by arc melting of the

* The term "fissia" refers to a synthetic mixture of oxides of stable isotopes representing fission-product elements in irradiated oxide fuel.

product. Oxidation rates were measured in 200 mm of oxygen. As observed in the earlier work, the freshly melted carbide was "unreactive." After five days of exposure to air saturated with water vapor, the material prepared from the 2.5 fissia mixture was reactive, whereas that prepared from 7.5% fissia was only partially activated. In tests with material prepared from 5.0% fissia, little oxidation of the fresh material occurred below 600°C. A second sample of this material that had been exposed to saturated air for three days ignited at about 405°C, but only about 15% of the material reacted; however, the sample reignited at 450°C and an additional 15% reacted. A third sample that had been exposed to saturated air for four days ignited at 325°C, but the reaction rate became negligible after about 25% of the uranium monocarbide had been oxidized. The results suggest that the presence of these concentrations of fission-product elements in uranium monocarbide decreases the rate at which the material is activated by exposure to moist air.

The oxidation of uranium monocarbide at 550 and 1000°C has been investigated by thermobalance measurements in which the off-gases were collected and analyzed.[92] The reaction appears to be incomplete at 550°C, since raising the temperature to 1000°C caused an additional weight loss of about 1%. Analyses of the product after oxidation at 550°C showed 0.2 wt.% carbon, some of which was identified as carbonate. A material balance based on the amount of carbon dioxide collected tended to confirm this result.

The reduction of uranosic oxide to uranium dioxide by carbon at low temperatures (< 900°C) has also been studied, using similar techniques.[91] Although the reaction proceeds approximately according to the equation

$$U_3O_8 + C \rightarrow 3UO_2 + CO_2 \qquad (5)$$

the results indicate that the stoichiometry is not exactly as indicated. The off-gases were found to contain about 1.5% carbon monoxide.

Further scale-up studies have been carried out on the oxidation of uranium monocarbide in a rotary furnace.[91] Approximately 1 kg of arc-melted uranium carbide (~ 5.2 wt.% carbon) was oxidized at 300 to 350°C in flowing air at ¼ to ½ atm pressure with a furnace rotation rate of 7 to 8 rpm. After about 3 hr under these conditions, temperatures up to 550°C and air pressures of up to 1 atm were employed. Oxidation above 300°C totaled 6 hr. A carbon dioxide analyzer on the exhaust gas stream proved to be a convenient device for monitoring the reaction. A sieve analysis of the uranosic oxide product gave the following results:

Mesh size	Wt.%
+50	0.2
−50 +200	2.0
−200 +400	9.7
−400	88.1

These results confirmed earlier laboratory-scale data. A sample of the −400 mesh fraction had a carbon content of 0.16%, a particle size of 3 μ (Fisher Sub-Sieve Sizer), and bulk and tap densities of 1.6 and 2.5 g/cm^3, respectively. A new screw conveyer to discharge the product from the furnace has been operated satisfactorily.[91] The oxide product can be removed from the furnace in less than 15 min.

Processing by the Carbide-Nitride-Carbide Cycle

It was reported earlier[95] that uranium monocarbide which has become reactive with nitrogen on exposure to moist air can be deactivated by annealing under vacuum at temperatures above 1000°C. Analyses of some material that had not been annealed showed oxygen and hydrogen contents of 1530 and 22 ppm, respectively, whereas the corresponding values for similar material annealed under vacuum at 1200°C were 805 and 4.5 ppm (Ref. 90). The annealed material was unreactive toward nitrogen.

The effect of annealing on surface area was examined in experiments with stoichiometric uranium monocarbide granules (−8 +30 mesh) that had been activated by exposure to water vapor. The results were as follows:[91]

Sample	Annealing treatment	BET surface area, cm^2/g
1	None	182
2	2 hr, 1200°C	160
3	2 hr, 1000°C	216
4	Sample 3; 2 hr, 1200°C	234

Although the treatment at 1200°C was sufficient to deactivate the material, no decrease in the surface area was evident.

Tests have also been conducted with hyperstoichiometric, stoichiometric, and hypostoichiometric* uranium monocarbide.[92] The "reactivity" was determined by the rate of nitrogen uptake by the material at 850°C. Deactivation by annealing was most rapid for the hypostoichiometric material, was less effective for the stoichiometric material, and essentially did not occur for the hyperstoichiometric material. In general, a good vacuum and a high temperature are required for effective deactivation.

The decomposition rates of uranium sesquinitride to the mononitride on heating in vacuum at temperatures from 650 to 1100°C have been determined and compared with similar data obtained previously from uranium sesquinitride–carbon mixtures.[92] This type of mixture is the product that is formed by the reaction of nitrogen with uranium monocarbide. In both cases the initial decomposition rate was constant (zero order). The overall reaction rate of the pure sesquinitride was lower than that of the mixture, but the rate per unit surface area was much higher. The probable reason for this is that the carbon increased the total surface area of the mixture without entering into the reaction. The apparent activation energies of the decomposition reaction were 64 kcal/mole for the pure sesquinitride and 91 kcal/mole for the sesquinitride-carbon mixture.

Electrolytic Process for Processing Uranium Carbide Fuels

Research has continued at Atomics International on the electrolytic process (described above) for uranium monocarbide fuel.[90–92] Studies of liquid-metal cathodes were continued. In one run a 20-g uranium monocarbide pellet was anodically dissolved in an equimolal LiCl-KCl melt containing 4 wt.% UCl_3, using a molten zinc cathode.[90] The anode and cathode efficiencies were 82%, the highest value achieved thus far with a liquid-metal cathode. Extrapolation of the results gave a zero-current potential of 0.2 to 0.4 volt. Previous work with a liquid cadmium cathode had given potentials of 0.9 to 1.1 volts.[96]

Additional studies have been made of the regeneration of uranium monocarbide from uranium amalgams[90–92] as the mercury is removed by distillation. Reaction of the uranium with propane, even at temperatures as low as 525°C, resulted in a product which contained over 6 wt.% carbon and which was probably a mixture of uranium monocarbide and free carbon. The addition of two parts of hydrogen to one part of propane at 550°C during a distillation resulted in a carbon content of the product of 5.80 wt.% but was not sufficiently effective to lower the carbon content to 4.80 wt.%, the theoretical value for uranium monocarbide. The use of methane, rather than propane, at 650°C resulted in a low carbon content (maximum, 2.60 wt.%). X-ray identification of the product from the propane reaction indicated the presence of uranium dicarbide, an interesting result, since the dicarbide had not been prepared previously at such low temperatures. No sesquicarbide has been found in the products. The results from four products that were obtained by distilling mercury from the amalgam in hydrocarbon atmospheres are summarized below:[92]

Hydrocarbon	Max. temp., °C	Carbon content, wt.%	Phases present (X-ray)
Propane	575	2.55	UC, U
Propane	750	9.50	UC, UC_2
Propane	525	6.45	UC, UC_2
Methane	650	2.60	UC, UO_2

Evidently, the last sample was partially oxidized, despite the use of an inert atmosphere during the handling operations. It was concluded that carbon content of the product is no more easily controlled when uranium amalgam is used as the starting material than it is when uranium powder is used. (R. K. Steunenberg)

* These designations refer to the carbon content of the carbide, i.e., greater than, equal to, and less than the theoretical carbon-to-uranium ratio of 1.00.

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Section

IV

Reactor Fuel Processing

Waste Disposal

Treatment of Liquid Wastes by Ion Exchange and Foam Separation

Ion Exchange

Oak Ridge National Laboratory (ORNL) is continuing to investigate the treatment of large volumes of low-level-activity process wastes that originate from many sources in the processing of nuclear fuels.[1–3] Two ion-exchange processes are being considered.[2] The development of a scavenging-precipitation ion-exchange process has progressed through a series of runs in a 600 gal/hr pilot plant.[1,2] In this process, precipitation of a portion of the activity with sodium hydroxide is carried out in a head-end treatment step, followed by clarification of the water in a gently agitated sludge-column clarifier unit. The clarified and filtered effluent is then passed through a carboxylic-phenolic resin for sorption of Cs^{137} and Sr^{90}. The results of the pilot-plant tests have shown this process to be capable of decontaminating 750,000 gal/day of low-level-activity ORNL plant waste to an activity level of less than 3% of the maximum permissible concentration (MPC) for water.[2] A new agitated clarifier (see Fig. IV-1) for the scavenging-precipitation ion-exchange process has been installed in the pilot plant to replace the nonagitated clarifier used in previous tests.[2,3] The purpose of the agitator is to promote precipitation of the hardness in the sludge blanket and to provide a better distribution of the solids in the blanket, thereby preventing channeling. Laboratory-scale tests of an agitated clarifier produced satisfactory precipitation and separation of hardness at throughput rates per unit area in the main blanket section of up to 60 gal/(hr)(sq ft), which is four times higher than throughput rates used in the nonagitated clarifier.

ORNL is also planning to investigate in the pilot plant a new ion-exchange process[2,3] that will be tested in fixed-bed and continuous countercurrent contactor equipment. In this ion-exchange process, two cation resin beds in series are used: a weak-acid resin followed by a strong-acid resin. The weak-acid resin removes the bulk of the calcium and magnesium and can be regenerated by dilute nitric acid in almost stoichiometric proportion to the exchange capacity of the resin. The strong-acid resin bed is thus free to sorb cesium, strontium, and other fission products and is regenerated with $5M$ HNO_3. This acid-regenerating solution which contains excess acid is used to regenerate the weak-acid resin bed at more frequent intervals. Decontamination factors of 1000 and 100 for strontium and cesium, respectively, are expected for this process. This process also has advantages over the scavenging ion-exchange process in that the chemical cost may be less for wastes that have less than 400 ppm of hardness.

Decontamination of Purex and Redox Plant Wastes at Hanford

At Hanford, ion-exchange techniques are being investigated for the removal of ruthenium and cesium from various Purex and Redox plant wastes.[4] Experiments were continued in the Micro Pilot Plant (MPP) to develop a process for the decontamination of Purex tank-farm condensate.[1] A run[4] was made to determine the removal of ruthenium by means of a thin precoat filter bed in which anion-exchange material of small particle size is used. Thus both filtration and anion-exchange adsorption could be done in one step. In this run a 5-cm-diameter by 1.5-cm-high bed of a strong base anion-

exchange resin (Dowex 1, 200 to 400 mesh) in the hydroxyl form was evaluated. Steam-stripped Purex tank-farm condensate was used for feed and passed through the precoat filter bed at a flow rate of 13.5 column volumes per minute [about 7 gal/(min)(sq ft)]. After about 3500 column volumes of the steam-stripped condensate had been treated, the precoat filter bed became saturated with nitrate and nitrite ions, and the removal efficiency for ruthenium decreased to about 84%. The concentration of Ru^{106} in the effluent did not exceed its MPC_w value for the entire run during which 9800 column volumes of steam-stripped condensate were treated. During the course of the run, the pressure drop across the precoat filter bed increased from 4 to 8 psi.

Laboratory ion-exchange experiments were also carried out to study the removal of cesium from Redox plant alkaline supernatant wastes.[4] In these experiments, simulated alkaline supernatant solution was passed through one Duolite C-3 cation-exchange column for 18 load-elution cycles. Each load-elution cycle was performed as follows: (1) load column to about 2% cesium breakthrough, (2) wash column with 3 column volumes of 0.01*N* NaOH, (3) elute sodium with 7 column volumes of 0.3*N* $(NH_4)_2CO_3$–0.1*N* NH_4OH solution, (4) elute cesium with 6 column volumes of 3*N* $(NH_4)_2CO_3$–1*N* NH_4OH solution, (5) backwash column with 2 column volumes of 2*N* NaOH, and (6) start load cycle again.

The cesium breakthrough curve for the 18th cycle was within experimental error of that of the first cycle. The principal problem encountered during the 18 cycles was the precipitation of aluminum hydroxide at steps where the *p*H dropped to less than 10. The precipita-

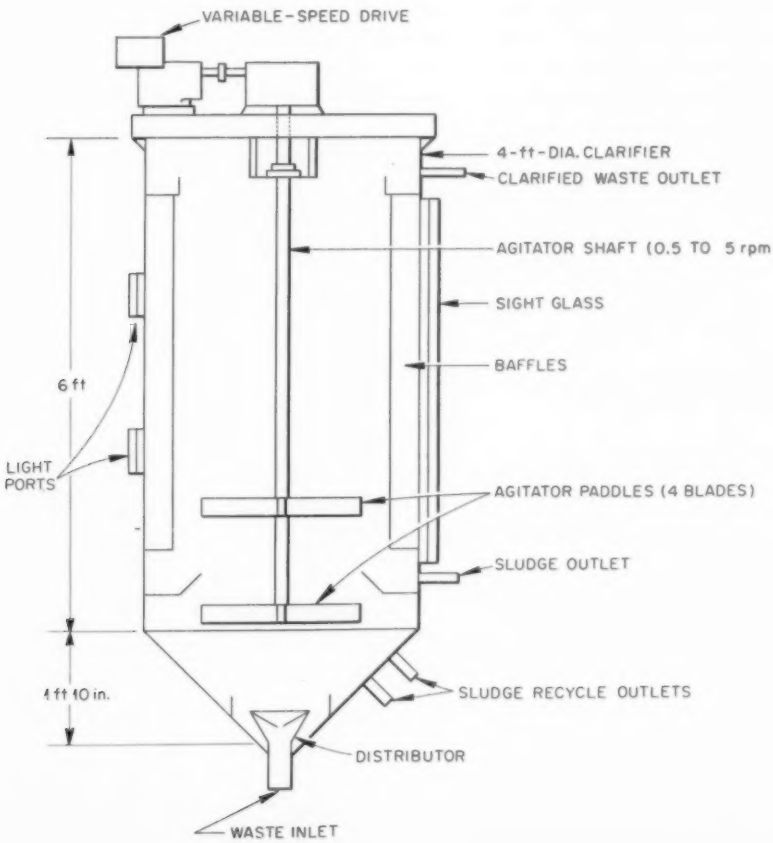

Fig. IV-1 Agitated clarifier for the low-level pilot plant.[3]

tion was minimized or avoided by substituting dilute sodium hydroxide for water washes. At the completion of the test, the ion-exchange resin was removed from the column, dried, and weighed to determine loss of weight. The weight loss of the resin was determined to be less than 5% after 18 cycles of use.

Foam Separation

Foam separation continues to be studied as a method for removing Sr^{90} from ORNL low-level-activity plant wastes (LAW).[5] Development work has proceeded over the past few years both at ORNL[2,3] and at Radiation Applications, Inc.,[6,7] under a contract with ORNL.

It has been shown[1] in laboratory tests that the presence of large amounts of calcium (60 to 70 ppm as $CaCO_3$) in the LAW interferes with the removal of Sr^{90} by foam separation. It is necessary then to precipitate a large fraction of the calcium (either as a carbonate or a phosphate) prior to foam separation. Two flow sheets (see Fig. IV-2) have been developed. The first, a two-step process [see Fig. IV-2(*a*)] involves the precipitation of calcium as the carbonate or orthophosphate in a slowly stirred, upflow sludge column that produces a clear effluent having a low calcium concentration (2 to 6 ppm as $CaCO_3$). This effluent (without filtration) is fed to a countercurrent, continuous foam column contactor. The second, a one-step process [see Fig. IV-2(*b*)] involves contacting the waste stream with precipitation-inducing chemicals (phosphate ion and ferric ion) plus surfactants [dodecylbenzene sulfonate (DBS) and Armeen Z] in a small mixing chamber, wherein calcium precipitates as the phosphate. Solids plus solution are then fed to a foam column, in which ionic contaminants are removed by the

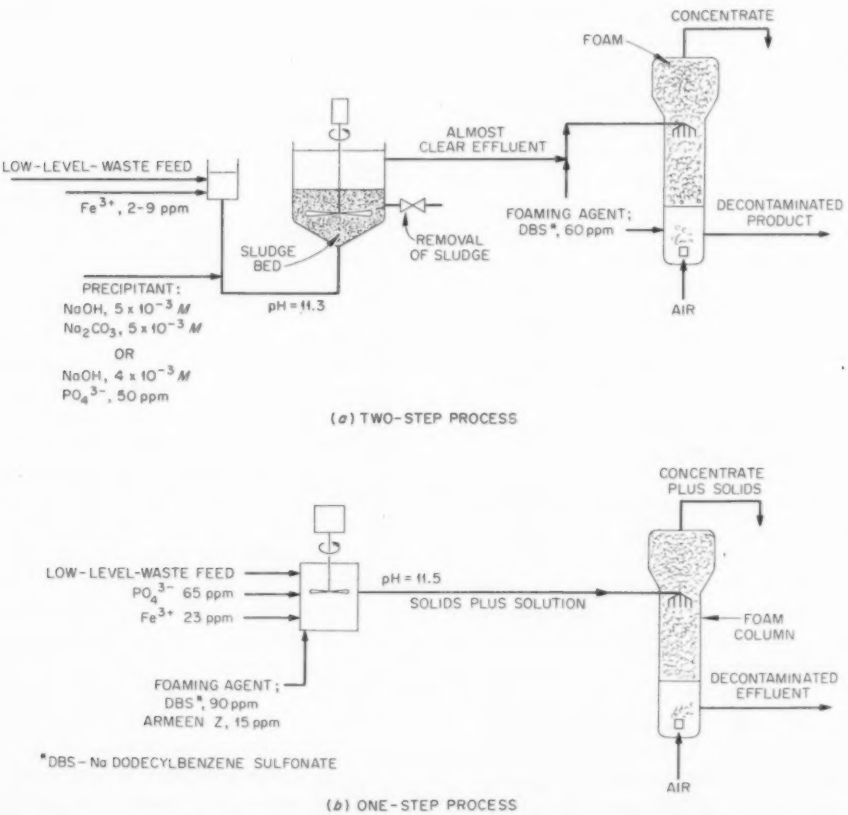

Fig. IV-2 The (*a*) two-step, precipitation foam-separation and (*b*) one-step flotation foam-separation processes.[2]

foam process, and the solids are removed by frothing or flotation. Both flow sheets are scheduled to be tested in the ORNL 600 gal/hr pilot plant.[2,3] A schematic flow diagram of the proposed pilot-plant equipment is shown in Fig. IV-3 (Ref. 2). For the pilot plant, a clarifier for removing calcium and magnesium by precipitation, a foam column, and two single surfactant (recovery) stripping stages were recommended.

Conversion of High-Level-Activity Wastes to Solids

Engineering-scale demonstrations of solidification processes which will be made with full-plant-level-activity wastes are to be carried out at Hanford in a pilot plant to be installed in the Fuels Recycle Pilot Plant, a new facility now under construction.[2,4] Prototype equipment for the demonstration of pot calcination, radiant-heat spray calcination (with or without continuous melting), and continuous phosphate glass processes is now being designed. The pot-calcination process is being developed at ORNL;[2] the radiant-heat spray calcination process at Hanford;[4] and the continuous phosphate glass process at Brookhaven National Laboratory.[8,9] The fabrication of all prototype parts with the possible exception of the prototype equipment for the continuous phosphate glass process is expected to be completed by the time that the construction of the Fuels Recycle Pilot Plant is scheduled for completion in June 1965 (Ref. 4).

A process equipment flow sheet[2] for the pot-calcination portion of the pilot plant is shown in Fig. IV-4. An induction furnace will be used for heating pots up to 12 in. in diameter and 6 ft long. The evaporator can be operated batchwise or continuously. Provision is also being made for collecting the pot condensate separately or for feeding it continuously by gravity to the evaporator. The overhead vapors from the evaporator will be condensed and then fractionated to produce water and nitric acid. The noncondensable gases will be filtered, passed through a silica-gel trap for ruthenium, scrubbed in a packed

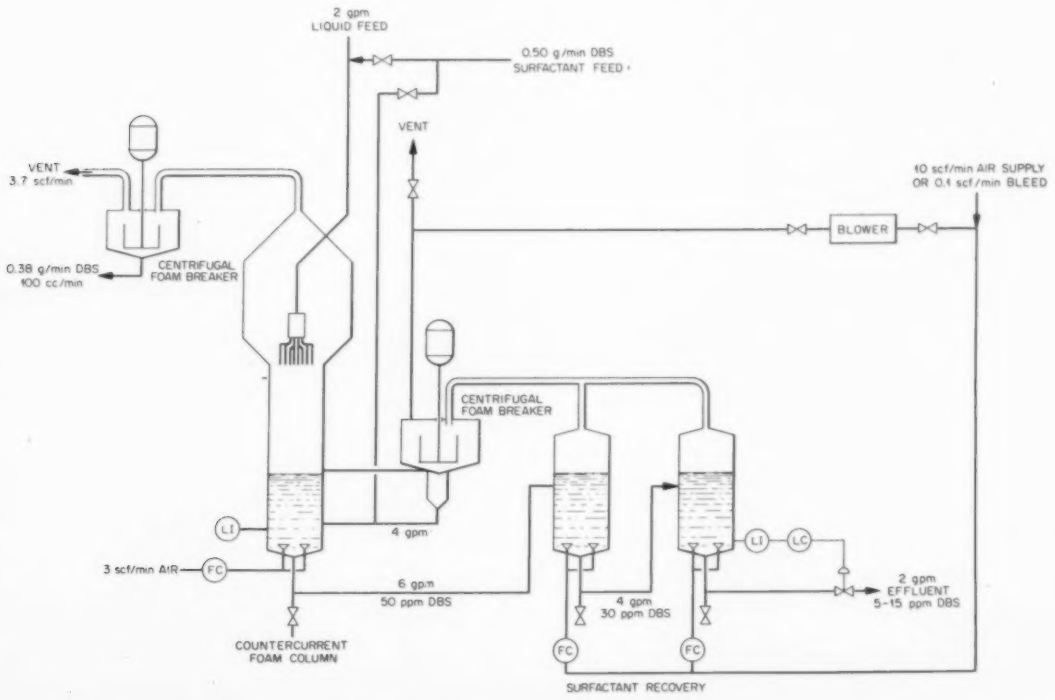

Fig. IV-3 Proposed low-level-waste pilot-plant foam column flow sheet.[2]

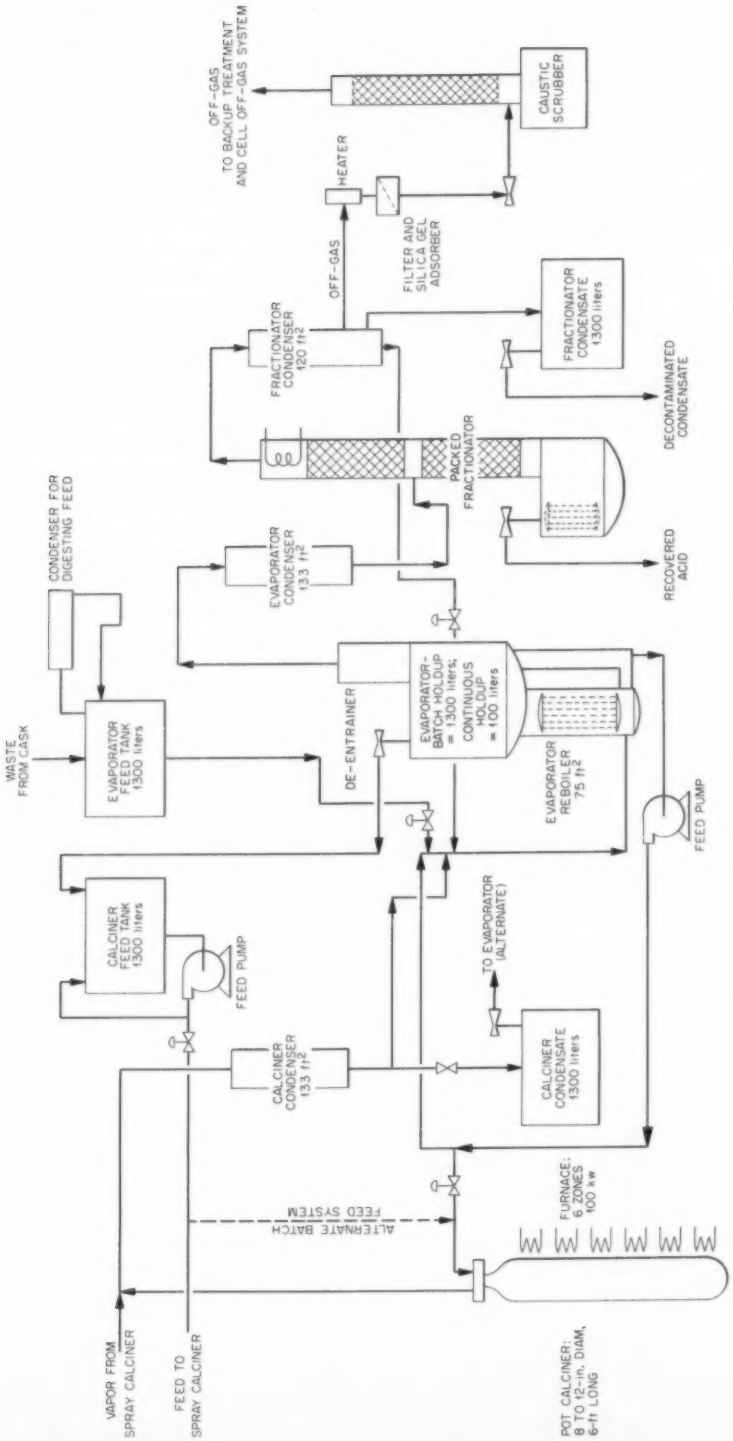

Fig. IV-4 Hanford pot-calcination pilot plant: flow diagram.[2]

tower, and refiltered before discharge into the cell-exhaust system.

The radiant-heat spray calciner will be operated using some of the components from the pot-calciner system, such as the external induction-heating equipment, the off-gas system, and the batch feed tank and feed pump. A layout of the major equipment items for the two calcination processes is shown in Fig. IV-5.

Recommendations of equipment and operating procedures for the demonstration of the pot-calcination process at the Hanford pilot plant are presented in an ORNL report by Hancher, Suddath, and Whatley.[10] This report does not present detailed data from the experimental engineering development program, which it covers; rather it gives the evolutionary justification for the recommended choices of equipment and operational techniques. Performance information is presented for equipment and system behavior and is based on engineering-scale studies of simulated Purex, Darex, and TBP-25 plant wastes.

Spray Calcination

Hanford is continuing to study radiant-heat spray calcination[11] as a method for the treatment of Purex-process high-level-activity aqueous wastes. In radiant-heat spray calcination, the feed solution is sprayed into the top of a heated column that is maintained at 700 to 750°C. Spray droplets are converted to solids, and some salt decomposition is achieved. The dried residue falls into a melt pot that is used to effect a reduction in volume of the residue. In the melt pot, which is maintained well above the melting temperature (typically 750°C) of the dried residue, further decomposition and melting of the dried residue take place continuously.

It was previously shown[11] that the volitilization of ruthenium from full-plant-level-activity Purex waste (1WW) could be suppressed by adjusting the acidic 1WW waste to *p*H 10 with sodium hydroxide and then adding sugar to the resultant alkaline waste. The decontamination

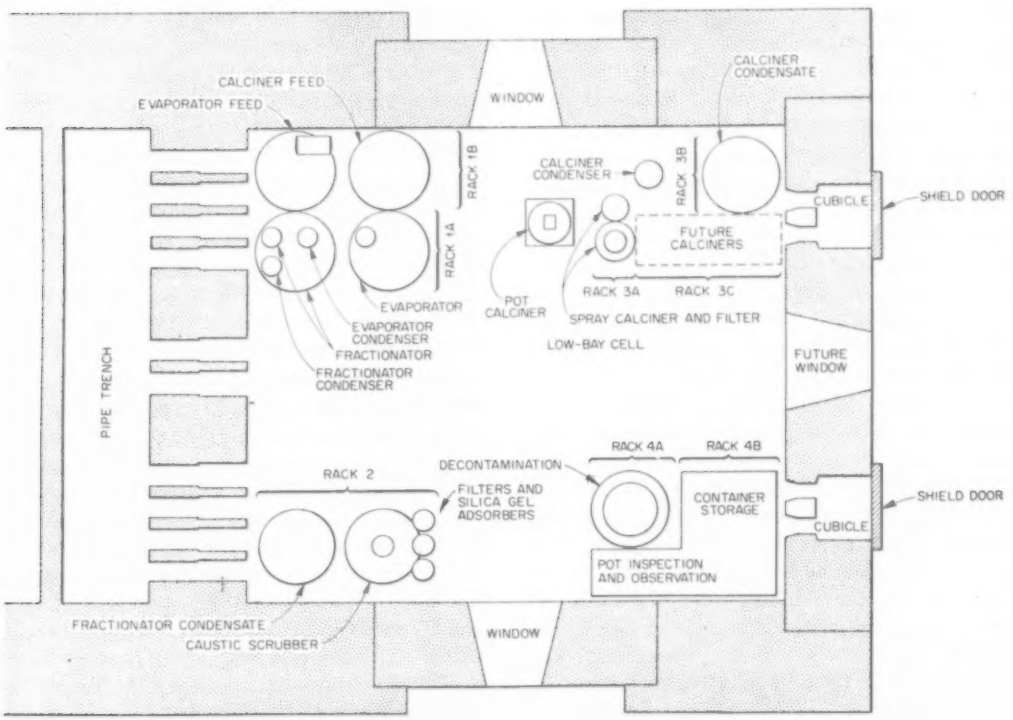

Fig. IV-5 Hanford pilot plant: vessel and rack arrangement.[2]

factor for ruthenium in this run was similar to that of the other fission products (about 1×10^9). In a recent spray-calcination run,[4] made with full-plant-level-activity 1WW, neutralization of the 1WW waste with ammonia instead of sodium hydroxide was investigated. If the same favorable suppression of ruthenium volatilization is obtained, neutralization with ammonia is expected to result in low calcine volume, since little or no stable solids would be added, and in potential reuse of the ammonia by recovery from the condensate. To produce a meltable calcine, sodium bisulfate ($0.72M$) was added as a fluxing agent before neutralization of the waste with ammonia. (No sugar was added in this run, although sugar is necessary for good calcination with wastes that are neutralized with sodium hydroxide.) Preliminary data showed that the ruthenium found in the condensate amounted to 1 to 2% of the original ruthenium present in the 1WW waste, which was greater than for the previous run in which the pH of the 1WW waste was adjusted to pH 10 with sodium hydroxide and to which sugar was added. However, it was much less than for spray-calcination runs made with acidic (1WW) wastes. On the basis of these results, effective suppression of ruthenium volatilization requires reducing conditions (e.g., addition of sugar) as well as basic conditions.

Several scouting spray-calcination runs were made with a nonradioactive, simulated Purex waste which had been formaldehyde treated (FTW) and which contained added calcium, sodium, and phosphate. These runs were carried out to determine if the radiant-heat spray calciner could be used to produce a product from this modified FTW waste which could be subsequently melted to form a phosphate "glass." Although the resultant feed was a slurry, it could be readily spray-atomized in the 18-in.-diameter by 10-ft-long cold semiworks spray calciner (with Mark II draft tube[1]). The powder produced in these runs melted to a free-flowing liquid below 950°C. Weight loss on melting (probably resulting from loss of sulfate) was less than 2%. However, there was some additional loss of sulfate upon holding the melt for extended periods at 950°C. Under these conditions the sulfate found in the condensate was less than 0.02%. Upon slow cooling, the material segregated somewhat; quenching did not produce a true glass structure, although no segregation of solid phases was evident.

In preliminary corrosion tests of Inconel, Hastelloy X, and stainless-steel type 310, specimens of these alloys were immersed in the molten phosphate glass material at 950°C. The corrosion rates for these alloys were observed to be less than 3 mils/month.

Fluid-Bed Calcination

The results of the final fluid-bed calcination run[12] in the testing of the 48-in.-diameter fluid-bed calciner at the Idaho Chemical Processing Plant (ICPP) Waste Calcining Facility[13] have become available. In this run, which lasted 700 hr, Na^{24} was added on two occasions to a synthetic aluminum nitrate feed solution [containing added boric acid ($0.01M$)] to determine the effectiveness of the off-gas cleaning system. Sand was used as the starting bed with a bed temperature of 400°C. The superficial fluidizing velocity was 1.0 ft/sec. The nozzle air-to-liquid volume ratios were varied during the run, from an initial 450 to a final 650. The feed rate was 60 gal/hr.

The performance of the off-gas cleaning system was considered excellent; activity measurements of samples of solids removed from the off-gas indicated a rate of release of solids with the ICPP stack gas of only 8×10^{-5} lb/hr, which is well below the tentative limit of 1×10^{-3} lb/hr. This tentative limit represents a release of 2 μc of Sr^{90} per second when calcining aluminum nitrate wastes (from an ICPP waste-storage tank designated as WM-185). This release of Sr^{90} corresponds to a ground-level atmospheric concentration of 2×10^{-10} μc/ml which is based on an estimated atmospheric diffusion factor of 10^4 from the ICPP stack to ground level.

With boric acid present in the feed solution, the product, as expected, remained essentially completely amorphous throughout the run; the alpha-alumina concentration in the product was less than 0.5% at all times. For amorphous material produced under these operating conditions, the bed material showed typical bulk, particle, and absolute densities of 0.95, 1.6, and 2.6 g/cm^3, respectively; the intraparticle porosity was 41%. The particle size of the bed material was effectively controlled by varying the nozzle air-to-liquid ratio. After the smaller-sized initial bed of sand had been replaced by calcined alumina, the mass median particle diameter in the bed was maintained in the

desired range of 0.55 to 0.60 mm; only two changes in nozzle air rate were necessary to effect this control. Process control was excellent; remote operation created no problems.

Pilot-plant calciner runs[12] were also made in the 2-ft-square fluid-bed calciner to investigate the effects of bed temperature on fines production and carry-over. At a nozzle air-to-liquid volume liquid ratio (NAR) at 250, the total rate of fines carry-over at a bed temperature of 300°C was double (3.7 kg/hr) the rate at 400°C (1.8 kg/hr) and triple the rate at 500°C (1.1 kg/hr). At an NAR of 500, the total rate of fines carry-over decreased from 3.7 to 2.7 kg/hr when the bed temperature was 300°C but increased from 1.1 to 2.7 kg/hr when the bed temperature was 500°C. These results appear to indicate that operation at a bed temperature of 300°C is not desirable for minimizing solids carry-over from the calciner. The rate of carry-over of solids was also shown not to be significantly affected by changes in mass median particle diameter of the bed over the range of 0.5 to 1.0 mm.

Phase transformation studies in the calcination of nitrates of aluminum, stainless steel, and Nichrome were carried out for the ICPP at the Stanford Research Institute.[12,14,15] In transformation studies[14] made on synthetic aluminas prepared from aluminum nitrate with various additives, boric acid and phosphoric acid were equally effective for prevention of formation of alpha alumina when the mole ratios of these additives to alumina were the same.[14,15] The results of tests on the effect of selected, simulated fission products on the formation of alpha alumina indicated that the rare earths and molybdenum tended to prevent the formation of alpha alumina, whereas barium, cesium, and zirconium either had no effect on alpha formation or aided it. Fission products at their expected concentrations should not, therefore, significantly affect the formation of alpha alumina or interfere with the use of boric acid to control crystallinity. The minimum temperature for formation of alpha alumina at moderate pressure was below 325°C.

The role of boron in retarding the formation of alpha alumina was studied. The results of this study indicated that the boron prevents crystallization of the alumina by forming a random distribution with aluminum atoms in a network of oxygen atoms rather than by combining with sodium to prevent the sodium from promoting the formation of alpha alumina. However, the results of other work carried out at the ICPP[12] show the existence of sodium-boron compounds resulting from the heating of sodium nitrate and boric acid at 500 to 530°C. These two conclusions probably are not in conflict, since the latter work[12] indicates the absence of sodium-boron compounds at both lower and higher calcination temperatures than the 500 to 530°C temperature range, and the presence of only small amounts of sodium-boron compounds in this range.

Transformation studies on stainless-steel wastes showed that alpha iron oxide would be formed even with the addition of moderate amounts of boric acid, phosphoric acid, aluminum, and combinations of these. Similar results were found for Nichrome wastes with nickel oxide being formed. Rare earths were the most effective additives for preventing the formation of alpha iron oxide in stainless-steel wastes.

Differential thermal analysis studies on nitrates of stainless steel and Nichrome showed that stainless steel formed oxides at a lower temperature than aluminum nitrate, whereas Nichrome required a higher temperature. A mixture of Nichrome and stainless-steel wastes acted like stainless-steel wastes.

In fluidization studies with a laboratory fluid-bed calciner, good amorphous alumina was produced from aluminum nitrate waste solutions. The operation of the calciner with stainless-steel nitrate wastes was not satisfactory, and the product contained alpha iron oxide. The addition of boric acid did reduce the alpha iron oxide content, but the product from pilot-plant operation is still likely to produce a product containing alpha iron oxide. The operation of the calciner with Nichrome wastes was very unsatisfactory. Crystalline nickel oxide was always formed in the product, even with the addition of boric acid.

Observations on the effect of additives on evaporation of aluminum nitrate solutions indicated that 0.6 mole of phosphoric acid per mole of alumina might be useful for pot calcination in achieving maximum bulk density of the product.

Vander Wall[16] at the ICPP has investigated the thermal decomposition of ferric nitrate nonahydrate, chromium nitrate nonahydrate, aluminum nitrate nonahydrate, and nickel nitrate hexahydrate, as well as the mixtures of these

compounds in the proportions produced in the dissolution of Nichrome and stainless-steel alloy nuclear fuels. The experiments were conducted in air at two heating rates, approximately 1.1 and 2.6°C/min. Chromium nitrate nonahydrate forms an intermediate mixed oxide with an empirical formula $CrO_{2.2}$ before decomposing completely to chromic oxide. Nickel nitrate hexahydrate forms several intermediate products during decomposition to nickel oxide with the principal intermediate, $Ni(NO_3)(OH) \cdot \frac{1}{2}H_2O$, occurring at 250°C.

The only crystalline material formed by the Nichrome mixture when heated to 450°C was nickel oxide. Owing to the presence of chromium, the stainless-steel mixture did not form crystalline material at 450°C. At 1000°C, all the above-mentioned compounds and mixtures of these compounds formed crystalline oxides.

Pot Calcination

At Hanford two pot-calcination runs[4,17] were made with full-plant-level-activity Purex waste (1WW) to determine the effect of adding calcium nitrate to suppress sulfate volatility and to evaluate the effect of excess sodium nitrate on cesium volatility and calcine stability. The equipment components for the treatment of the off-gas in these two runs consisted of a condenser and Cambridge absolute filters.

In the first run, sulfuric acid was added to the 1WW waste (to a total sulfate concentration of 0.88*M*) in order to simulate high sulfate conditions. Immediately prior to calcination, calcium nitrate (in slight excess of the stoichiometric requirement) was added. Twenty liters of the modified waste solution was then calcined. The resulting calcine did not melt. No operational difficulties were encountered during the run. Volatilization of sulfate to the condensate was less than 0.05% as compared with 1.3% in an earlier run[18] in which magnesium was used to suppress sulfate volatility; in both runs the behavior of ruthenium was essentially the same, about 15% of the original ruthenium present in the 1WW appearing in the condensate. A large increase in the radioactivity in the off-gas occurred during the final drying period of the run (shortly after the feed was turned off). It was thought that the lack of condensing steam during this period prevented the condenser from operating efficiently. Additional saturated steam was then fed to the off-gas line ahead of the condenser during the final drying and calcining period of this run. This procedure was not effective, since an increase in the radioactivity in the off-gas occurred despite the addition of more steam. The increase was of the same order of magnitude as that obtained in runs without added steam.

In the second run, 10 liters of 1WW waste with sodium nitrate added (1 mole $NaNO_3$ per liter of 1WW waste) was calcined. The resulting calcine melted. During the final drying and calcining period of the run, an increase in the radioactivity in the off-gas was again observed. Ruthenium was the predominant activity; however, the amount of cesium in the off-gas was also extremely high, as compared with its behavior in low-sodium runs. The decontamination factor for cesium in the post-condenser off-gas dropped from a value of over 10^7 to about 600 during this period. Cerium and zirconium did not show as large a decrease in decontamination factor during this period, which indicates that cesium is preferentially driven off under these conditions. Although this may have resulted from its higher volatility, it is also possible that, with high concentrations of sodium nitrate, cesium remains in the concentrated salt solution in the pot to the end of the run (while most of the other fission products precipitate). Thus cesium may be driven off in relatively large amounts by spattering which occurs during the final drying step. The high-efficiency filters in the off-gas train contained, to a decontamination factor of greater than 10^6, the increase in radioactivity which occurred during the final drying and calcining period of the run. During storage of those calcine pots in which 1WW wastes containing excess sodium were calcined, positive pressure (1 to 2 psig) has developed. Therefore a deficiency of stable anions (such as sulfate, carbonate, and phosphate) appears to be detrimental to pot calcination, both in terms of cesium off-gas decontamination and long-term storage stability.

Pot-Calcination Studies at ORNL

ORNL is continuing its investigation of the pot-calcination process for converting high-level-activity wastes to solids.[2,19] Laboratory and engineering-scale studies[2] are being carried out to provide design information for a pilot plant to be constructed at Hanford. Experimental work has been carried out with simulated TBP-25, Darex, and Purex 1WW and

Table IV-1 COMPOSITIONS AND CHARACTERISTICS OF SIMULATED HIGH-LEVEL WASTES[2]

Constituent	Waste compositions, moles/liter			
	TBP-25	Darex	Purex 1WW	Purex FTW-65*
Al^{3+}	1.72		0.1	0.05
Fe^{3+}		1.25	0.5	0.10
Cr^{3+}		0.38	0.01	0.02
Ni^{2+}		0.18	0.01	0.01
Hg^{2+}	0.02			0–0.0035
Mn^{2+}		0.04		
Na^{+}	0.1		0.6	0.3
NH_4^{+}	0.05			
H^{+}	1.26	2.0	5.6	0.5
Ru	0.002	0.002	0.002	0.002
SO_4^{2-}			1.0	0.15
PO_4^{3-}				0.005
SiO_3^{2-}				0.01
F^{-}				0.0005
Cl^{-}		0.001		
NO_3^{-}	Bal.	Bal.	Bal.	Bal.
Density, g/ml	1.32	1.33	1.30	
Gal/ton of U	106†	24†	40	82

*Purex FTW-65 which is expected to be produced at Hanford in 1965 is different from current Purex 1WW in that it will have been treated with formaldehyde to reduce the nitric acid concentration.

†Gallons of waste per kilogram of U^{235} processed.

FTW-65 plant wastes (see Table IV-1). The pot-calcination process involves introducing the waste into an evaporator, where it is concentrated and where nitric acid is steam stripped by the addition of water. This concentrated solution is then fed into a heated calciner pot (with a constant liquid level), where the waste is denitrated, brought to a solid cake, and calcined in place. Large amounts of gases are neither introduced nor produced, and the off-gas volume from the process is very low (1 or 2 cu ft per liter of feed) and results primarily from inleakage and instrument probes. The calciner pot of solids is then disconnected from the system, sealed, and used as the container for the waste during final storage at a suitable site. Studies made thus far indicate that special salt mines[20] may be the most suitable sites for this purpose.

Batch and continuous evaporation process flow sheets are being tested. In the batch evaporation process (see Fig. IV-6), the tanks and evaporator are large enough to accommodate enough waste to fill one pot. The calciner pot is fed from a tank of concentrated waste either by gravity or by pumping. Concurrently, the condensed vapors from the pot are returned to an evaporator filled with the waste for the next batch, which is undergoing concentration and acid removal. In the continuous evaporation process (see Fig. IV-7), a smaller evaporator is used and the condensed pot vapors are returned to the evaporator, from which the feed to the pot is pumped. This evaporator is fed with raw waste and continuously removes the nitrate from the system. The batch evaporation flow sheet offers the advantage of simplicity of control and operation but has disadvantages because of larger equipment and larger holdup. The continuous evaporation flow sheet has the advantages of smaller holdup, smaller equipment, and more reasonable application to a plant with several pot lines fed from the single evaporator. The control of the continuous evaporator is more complex, however, since the flow sheet is not truly continuous in that the pots are filled batchwise, and the evaporator must follow the transient filling of the pot.

The results[2] of 11 engineering-scale tests which were made with simulated TBP-25 and Purex FTW-65 wastes are presented in Table IV-2. In these runs, 8-in.-diameter by 90-in.-high pots of type 304L stainless steel were used. Feeding the calciner pot by gravity feed (gravity head of 10 ft) was shown to be a satisfactory alternative to pump feeding. In three runs a small amount of monobutyl phosphate and dibutyl phosphate (MBP and DBP) was added to the feed to simulate tributyl phosphate (TBP) degradation products possibly present in some high-level-activity wastes. The organic additives promoted foaming, but not to a detrimental extent.

In the TBP-25 calcination runs, the variation in feed volume to the pot (see Table IV-2) is primarily an operational variable and could have been made more consistent. The water-to-feed volume ratio, the amount of water necessary to strip the nitric acid from the evaporator, should be about 2.3. Higher values indicate an unnecessarily low set point for the acid in the evaporator overhead. The feed to the pot is more concentrated than the original waste feed to the evaporator. The feed to the evaporator contains about 23 g of aluminum per liter, and the feed to the pot contains 45 to 55 g of aluminum per liter. A successful run was made in which the calciner feed contained 115 g of aluminum per liter (see Table IV-2,

run 65), but the use of the more concentrated solution is considered because the solution will crystallize at room temperature. The average system feed rate was 20 liters/hr, with a maximum of 26 and a minimum of 17.

The nitrate concentration remaining in the solids depends on the calcination time. After 20 hr of calcination, the residual nitrate was reduced to acceptably low levels. In all cases the low levels are characteristic of the bulk of the cake, and the high levels represent the center top part of the calciner product.

Bulk densities of about 0.62 g/cm^3 were achieved with TBP-25 waste. The bulk density is defined as the ratio of the weight of solids in the pot to the volume of the pot up to the liquid-level point, including the void that occurs in the center.

The behavior of mercury during tests with TBP-25 waste was of interest since mercury compounds are unstable at 900°C, and volatilized mercury must be removed from the system. A cyclone trap for removing mercury compounds from the calciner off-gas stream was installed but was only partially effective. The calciner off-gas line was heated to 400 to 500°C, while the trap was maintained at about 150°C for condensation of mercury compounds. On the average, the trap contained 19% of the mercury, the evaporator about 40%, and the solids in the calciner about 13%. The remainder deposited on the process piping and equipment throughout the system.

In the tests with FTW-65 waste, the large feed volumes (see Table IV-2) reflect the diluteness of the feed. Since the initial iron concentration was about 12 g/liter, the evaporator concentrated the feed three- or fourfold, and the water-to-feed volume ratio was less than 1. The average feed rate varied from 26 to 68 liters/hr. The nitrate in the residual solids was reduced to an insignificant level by adequate calcination time, and the bulk density was about 1.3 g/cm^3. The cyclone trap was employed with little success in condensing the volatilized mercury from the FTW-65 wastes. However,

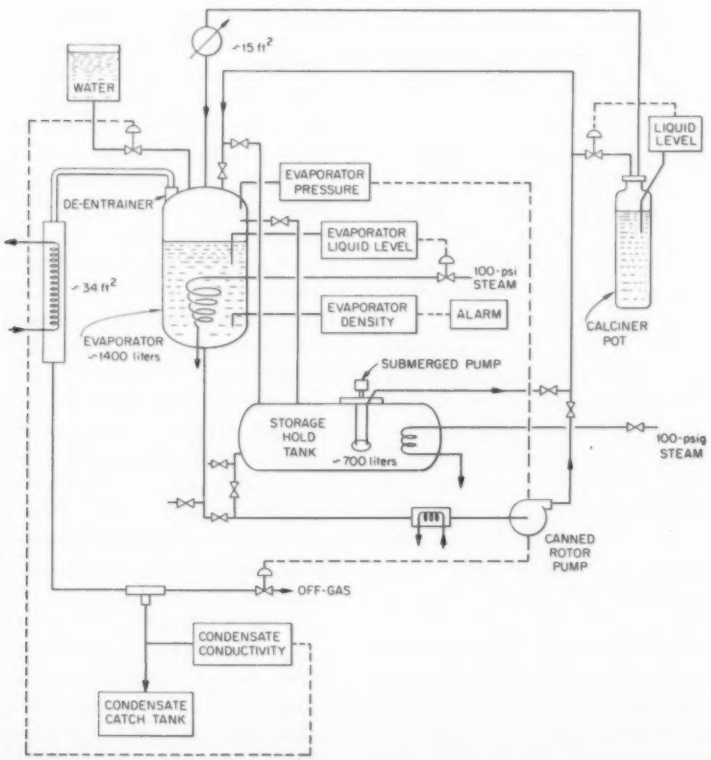

Fig. IV-6 Flow sheet for engineering batch evaporation tests for pot calcination.[2]

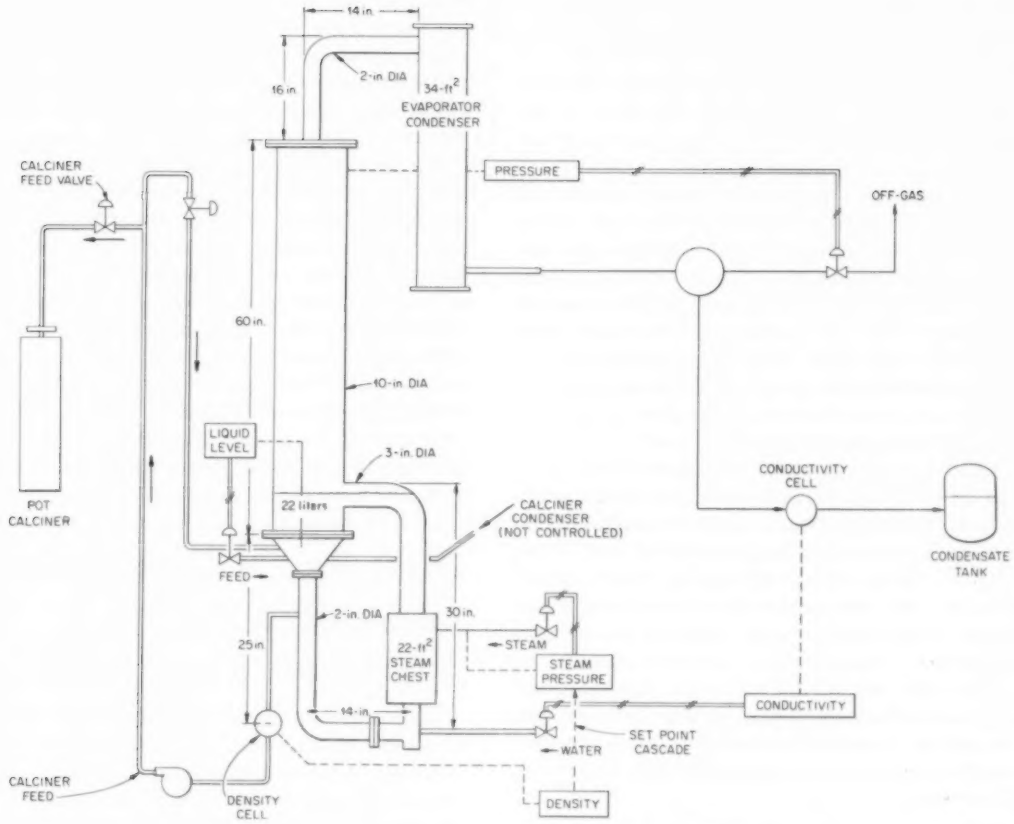

Fig. IV-7 Flow sheet for engineering continuous evaporation tests for pot calcination.[2]

Table IV-2 SUMMARY OF ENGINEERING-SCALE TESTS[2]

Run No.	Feed type	Calciner feed Al^{3+} or Fe^{3+} concentration, g/liter		Feed volume, liters	Water-to-feed volume ratio	Average system feed rate, liters/hr	Nitrate remaining in solids, wt.%	Solid bulk density, g/cm³
		Al^{3+}	Fe^{3+}					
65	TBP-25	115.5		476	3.1	20.6	0.19–0.06	0.68
66	TBP-25	55.0		449	6.4	20.4	0.04	0.65
67	TBP-25	45.1		391	2.8	17.0	0.007	0.50
68*	TBP-25	47.5		343	2.6	26.4	0.019	0.54
69*	TBP-25	45.0		469	5.4	15.6	0.111	0.64
70	FTW-65		46.9	1818	0.75	67.3	0.04–0.01	1.25
71	FTW-65		34.6	1843	0.57	68.3	0.02–0.01	1.30
72	FTW-65		26.7	1912	0.10	40.0	0.026–0.004	1.33
73†	FTW-65		40.2	1838	0.20	31.1	0.103–0.006	1.23
74†	FTW-65		49.2	1968	0.34	53.0	0.016–0.015	1.30
75	FTW-65		33.8	1793	0.72	26.0	0.01	1.26

*Gravity feed.

†1 ml of 50% monobutyl phosphate–50% dibutyl phosphate is added per 200 liters of feed.

the feasibility of removing mercury from these wastes by amalgamation with copper was demonstrated on a laboratory scale.[3,21]

In the tests with FTW-65 waste containing 0.005*M* fluoride ion, severe corrosion of the calciner pot was encountered even in the presence of calcium which was added (as the nitrate) to reduce sulfate volatilization (Refs. 2, 3, and 21 to 23). Little corrosion was observed in the absence of fluoride. The procedure for the addition of calcium was modified to ensure precise, continuous addition and hence a uniform action to retain sulfate and reduce corrosion by fluoride. The maximum fluoride concentration expected in FTW-65 waste is 0.005*M* (see Table IV-1), and satisfactory corrosion rates are expected at this concentration.

ORNL is planning to demonstrate the pot-calcination process on a semi-pilot-plant scale (10- to 30-liter scale), using radioactive wastes obtained from the Hanford Purex and Idaho TBP-25 plants.[2] Ten calcination, three glass-fixation, and five evaporation experiments are planned. In addition, one experiment will be made with a Purex plant waste containing no sulfate. The loaded calciner pots, after cooling, will be disconnected, equipped with instruments to monitor temperature and pressure, and then transferred to a storage site for long-term observation.

Hanford Denitration Tests of Purex Acid Wastes with Sugar

Because the use of formaldehyde requires rather elaborate process and equipment control systems for safe operation, Hanford is carrying out plant-scale tests in which sugar (sucrose) is being tested as an alternative for formaldehyde as a denitrating agent for Purex plant nitric acid wastes.[4,24–26] The results of extensive laboratory, hot-cell, and engineering-scale pilot-plant studies have shown sugar to be a simple and effective denitrating agent.[24–26]

In the reaction of nitric acid and sugar, about 20 moles of nitric acid is decomposed for each mole of sugar consumed. The utilization efficiency is not appreciably affected by acidity or temperature, but it is somewhat dependent on the concentration of certain catalytic ions, such as ferric ion. The threshold temperature for initiation of the reaction is about 85°C. All reaction products are gaseous (oxides of nitrogen and carbon); no residual tars or organic compounds are formed. Nitric acid can be recovered from the off-gases by use of a conventional downdraft condenser; however, unlike formaldehyde, use of a reflux tower on the reaction pot does not improve the overall sugar utilization efficiency. Other sugars and syrups (such as "black strap" molasses) have also been used successfully.

Both batch and semicontinuous operation were found to be practical; however, the simpler batch operation method is being tested on the plant scale. In batch operation a concentrated sugar solution sufficient to accomplish the desired degree of denitration is added to a batch of concentrated Purex acid waste (typically 2500 gal in a 5000-gal tank), and the contents are heated to boiling for 12 to 24 hr. The reaction is smooth and easily controlled (by the rate of heating). In semicontinuous operation, feed and sugar are added continuously to a heated tank, but the tank is emptied batchwise.

Land Burial Operating Experience at Savannah River Plant

The burial ground at Savannah River consists of approximately 83 acres which are located near the center of the plant area between two chemical separations areas.[27] Surface relief in the burial ground is low with a maximum difference in elevation of 22 ft. No flowing streams cross the area. The annual rainfall is 45 to 50 in.; surface runoff is through three drainage ditches. Underlying sediments are typical of the Atlantic coastal plain, consisting of sands, sandy clay, and clay beds with a predominance of sandy clays. The depth of these unconsolidated deposits above the hard metamorphic basement rocks ranges from 900 to 1000 ft. The average depth of the water table in the burial area is 40 ft. There are also some small water-saturated zones, perched above the normal water table on supporting clay beds.

Containment is the basic radioactive waste management policy. Ground disposal has always been limited to the burial of solid waste and the discharge of very-low-level-activity liquid waste to seepage basins. Solid waste accounts for the major portion of the radioactive materials disposed of in the ground since plant startup in 1953.

Solid radioactive waste is placed in unlined trenches excavated 20 ft into the soil. Trenches

filled with waste are backfilled with at least 5 ft of earth. Waste is primarily sorted and buried according to the type of radiation emitted, i.e., alpha or beta-gamma. Beta-gamma emitting waste is further divided into high- and low-level waste (less than 100 mrad/hr at 3 in. in low-level waste). The land burial of solid radioactive waste from 1953 to the end of 1961 has amounted to some 577,000 curies of fission products and induced radioactivity and 180 curies of alpha waste. These estimates were based, in part, on the radiation intensity of the waste at the time of burial and do not include correction for decay since burial. Routine monitoring of ground water at 13 wells since 1956 has never indicated above background levels of radioactivity.

To determine the extent of radionuclide migration into soil beneath the burial trenches and to evaluate potential migration, a comprehensive study was begun in 1961. Soil samples for radionuclide analyses were collected from 79 auger holes and 16 cored holes. Seventeen augered holes were located just off the side of the backfilled trenches. All others were in the center of the trenches and extended into the undisturbed soil beneath. These samples contained only very small quantities of radionuclides, particularly Cs^{137} and $Sr^{89,90}$. At one location where perched water is present to provide the hydraulic drive, the radioactivity was displaced downward 7 ft into undisturbed soil. This was the maximum migration observed during the investigation. At this location, 9 ft of soil remains between the radionuclides and the water table. Should radionuclides enter the water table at the burial ground, they must traverse a flow path over 1 mile long before outcropping at the surface on the floodplain of a Savannah River tributary. A velocity measurement (using tritium as a tracer) for the flow path indicates a travel time for ground water in the flow path of 125 to 200 years. It is therefore expected that very little, if any, buried radionuclides will enter public zones.

Recovery of Fission Products

ORNL has continued its investigation of a process (Phenex)[28] for recovering cesium from alkaline solutions. This process involves extracting the cesium with substituted phenols and stripping it with dilute acid. This process has been demonstrated successfully in batch or batch countercurrent tests with (1) simulated Hanford Purex wastes after adjusting with tartrate and sodium hydroxide, (2) Hanford tank-farm supernatant solutions, and (3) sodium hydroxide digests of ammonium molybdophosphate that had been used as a cesium adsorbent.[29] Since the phenols are highly selective for cesium, excellent decontamination is obtained from other fission products, bulk contaminants of the solutions, and other alkali metals.

Continued screening[2] of a large number of phenols of varying structure revealed several with extraction characteristics superior to those of *p*-dodecylphenol, *o*-phenylphenol, and 4-chloro-2-phenylphenol which have been described previously.[28] Best performance was given by 4-chloro-2-benzylphenol (commercially available as Santophen-1) and 4-*sec*-butyl-2-(α-methylbenzyl)phenol (BAMBP).[2] The latter extractant is especially attractive owing to its low reactivity with sodium hydroxide, low loss to the aqueous phase, and compatibility with a wide selection of diluents.

In a batch countercurrent test with Santophen-1 in diisopropylbenzene diluent, greater than 99.7% of the cesium was recovered from simulated Purex 1WW waste (tartrate complexed and adjusted to *p*H 12.3) in six extraction and two scrub stages.[2] The aqueous feed to organic ratio was 2 to 1, and the extract was scrubbed with one-third its volume of a 0.01*M* NaOH–0.002*M* sodium tartrate mixture. Acid was added to the last extraction stage to minimize phenol loss to the aqueous phase. The scrubbed extract was stripped quantitatively in a single contact with 0.05 volume of 0.1*M* HNO_3 to give a product solution containing 4.9 g of cesium and 0.035 g of sodium per liter. The overall cesium-to-sodium decontamination factor for the experiment was about 6×10^4.

Laboratory studies of a three-cycle solvent-extraction process[30] for recovering strontium and mixed rare earths with di-(2-ethylhexyl) phosphoric acid (D2EHPA) from Purex 1WW waste have also continued at ORNL. In further evaluation of this process, batch countercurrent runs were made to investigate the separation of rare earths from yttrium.[2] The runs were carried out with 0.3*M* D2EHPA–0.15*M* TBP-Amsco 125-82 that had been loaded with rare

earths and yttrium (traced with Eu^{152} and Y^{91}). In tests simulating the first cycle, 98.5% of the europium, but only about 5% of the yttrium, was stripped with 1.2*M* HNO_3 in five stages at an organic-to-aqueous flow ratio of 5 to 1. Since most of the fission-product rare earths are stripped more easily than europium, stripping recoveries of the total rare earths would be higher in actual practice. Nearly the same results were obtained in tests simulating the second cycle. The results indicated that yttrium contamination of the mixed rare-earths product could be limited to less than 2% of the amount in the original waste solution. Following stripping of rare earths, yttrium can be recovered from the solvent with 3*M* to 4*M* HNO_3.

Additional data[2] have been obtained at ORNL which showed that nitric acid, iron sulfate, and certain fission products can be removed from Purex wastes by amine extraction to produce aqueous feeds that are more amenable to the recovery of strontium and cesium. These data confirm previously reported results.[28] In a test with simulated Purex 1WW (4*M* H^+), a single contact with 0.24*M* Primene JM in Amsco 125-82 at an organic-to-aqueous phase ratio of 15 to 1 resulted in the extraction of about 90% of the nitric acid. This treatment also removed 72% of the ruthenium and 40% of the zirconium-niobium, but less than 3% of the iron, strontium, and cesium, from the waste. Except for the ruthenium and zirconium-niobium content, the resulting aqueous solution is similar in composition to that produced in the process proposed for use at Hanford wherein the Purex 1WW waste is treated with formaldehyde to destroy nitrate.

In a test using simulated formaldehyde-treated Purex waste (0.2*M* H^+, 0.5*M* Fe), the extraction of iron and acid was demonstrated in a batch countercurrent test with 0.24*M* Primene JM (80% in sulfate salt form) in Amsco 125-82 (Ref. 2). About 94% of the iron was extracted in two extraction stages and one water scrub stage, whereas only about 5% of the cerium was extracted. The aqueous feed to organic to scrub flow ratios for the test were 1 to 9 to 0.5. Although zirconium-niobium and ruthenium extractions were not followed, these elements would be expected to be almost completely removed along with the iron. More than 98% of the cerium was extracted by contacting the raffinate (*p*H of about 1) with six successive volumes of 0.24*M* Primene JM in Amsco 125-82 at an aqueous-to-organic ratio of 10 to 1, leaving a raffinate that would be highly amenable to treatment for strontium and cesium recovery.

ORNL also continued its investigation of the recovery of strontium and rare earths from Purex 1WW by ion exchange[2,20] and a head-end double precipitation step prior to ion exchange.[31] The ion-exchange recovery of fission products from Purex wastes is hindered by the large concentration of iron present. The sorbed ferric ion would precipitate in the resin bed during the elution cycle in which rare earths and strontium were recovered at *p*H greater than 3 (Ref. 21). Oxalic acid added to the waste solution effectively complexed the iron and eliminated its sorption on the resin bed. However, precipitation of other sorbable cations, such as rare earths, strontium, and barium, did occur as they displaced hydrogen ions of the resin, i.e., release of hydrogen ion from the resin lowered the acidity of the local exchange zone to $0 < pH \leq 1$, where, according to solubility data, oxalates of these cations are very insoluble. Consequently, another complexing agent, citric acid, was evaluated.

Distribution coefficients for Ce^{3+}, Sr^{2+}, and Fe^{3+} in simulated Purex 1WW waste were determined as a function of dilution of the 1WW waste. The waste solution was pretreated by adding 1.5 moles of citric acid per mole of Fe^{3+}, Al^{3+}, and Cr^{3+} and by neutralizing to *p*H 2.5 with concentrated ammonia. The cation-exchange resin (Dowex 50W-X8; 100 to 200 mesh) was preequilibrated with 0.5*M* HNO_3–0.005*M* ammonium citrate at *p*H 2.5. The data from the determinations of the distribution coefficient show that citrate in the acidity range 0.1*N* to 1.1*N* accomplishes the desired complexing of Fe^{3+}. At the same time, citrate allows the sorption of Ce^{3+} and Sr^{2+} on the ion-exchange resin, provided that the dilution of the waste is greater than 10. At a dilution of 20, the separation factors for strontium and cerium from iron were greater than 200 and greater than 600, respectively; and for cerium from strontium, about 3.

In two ion-exchange runs, simulated Purex 1WW which was diluted twentyfold, citrate treated, and contained added activity (Sr^{85}, Ce^{141}, Ba^{133}, Ca^{47}, and Fe^{59}) was passed through a Dowex 50W-X8 (100 to 200 mesh) resin. The results largely substantiated the distribution coefficient values described above. In addition, major separation of rare earths, calcium, strontium, and barium from each other was

achieved by elution with ammonium α-hydroxyisobutyrate[32] at successive concentrations of 0.48M, 0.8M, 1.0M, and 2.0M, respectively. These results show that up to 67 resin volumes of diluted (twentyfold) Purex 1WW (equivalent to 3.3 volumes undiluted Purex 1WW) could be processed for strontium and rare-earth recovery per volume of Dowex 50W-X8 (100 to 200 mesh) resin.

In an experiment[21] to evaluate the use of citrate ion as a complexing agent in the head-end double precipitation and ion-exchange process for the recovery of strontium, Dowex 50W-X8 (100 to 200 mesh) resin and the simulated Purex 1WW (5.6M H^+) were pretreated as described in the distribution coefficient study above. The head-end double precipitation treatment (which produces a strontium concentrate for processing by ion exchange) consisted of adding excess ferric ion, precipitating sulfate ion at 55 to 60% HNO_3, reducing the volume of filtrate by distillation, adding 90% nitric acid to the filtrate to precipitate strontium at greater than 85% HNO_3, filtering, and dissolving the strontium precipitate in a minimum amount of water. The volume of the strontium concentrate is about one-third the volume of the original 1WW. On the basis of the results of strontium recovery, it was tentatively concluded that, coupled with a head-end double precipitation step, up to 66 volumes of undiluted Purex 1WW can be processed per volume of cation-exchange resin. This is equivalent to processing 20 times more (undiluted) Purex 1WW per volume of resin than by an ion-exchange process which does not include a head-end treatment step.

(Phillip Fineman)

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Section

V

Reactor Fuel Processing

Production of Uranium, Thorium, Plutonium, and Their Compounds

Production of Uranium Dioxide

Reduction of Uranium Trioxide

Gas-solid reactions, particularly the reduction of uranium trioxide to uranium dioxide with hydrogen and the hydrofluorination of uranium dioxide to produce uranium tetrafluoride, are important steps in the production of both uranium metal and uranium hexafluoride. The rate of these reactions has been shown to be determined by the structure of the solid surface which, in turn, is modified as the reactions progress. Galkin and associates[1] have made an assessment of the thermodynamic characteristics of several agents which could be employed to reduce uranium trioxide to uranium dioxide. As a result of this study, it was observed that the reducing properties of carbon monoxide are superior to those of hydrogen. However, the reducing properties of CO vary inversely with temperature; this might be explained by a shift in the equilibrium between CO and CO_2.

Preparation of Reactive Uranium Dioxide

The reactivity of uranium dioxide toward hydrofluorination depends on its physical properties (particle size, porosity, and surface area) which, in turn, are governed by the origin and structure of the parent uranium trioxide. The kinetics of the reduction reaction (i.e., reduction of uranium trioxide to uranium dioxide) also affect the reactivity of the uranium dioxide product. As a result, uranium dioxide of widely differing reactivity may be prepared. It has been observed[2] that, when uranium trioxide which has been produced by spray denitration of uranyl nitrate hexahydrate in a fluidized-bed reactor is reduced by hydrogen, a relatively unreactive grade of uranium dioxide is the product. One observation that is of commercial importance in the processing of uranium oxide produced in fluidized beds is that the reactivity of uranium dioxide toward hydrofluorination may be markedly enhanced by the addition of 0.1 to 0.5% sulfate to the uranyl nitrate feed solutions. To aid in the understanding of the mechanisms that govern the reactivity of solid materials in gas-solid reactions, Ellis and Paton[3] have investigated the behavior of sulfate during the hydrogen reduction of sulfated uranium trioxide. In tests in which hydrogen was passed at 500°C over uranium trioxide containing 1000 ppm sulfate, it was observed that the sulfate was eliminated from the UO_3 exclusively as hydrogen sulfide. The reaction of hydrogen with pure uranyl sulfate at 500°C was observed to proceed rapidly, with hydrogen sulfide being immediately evolved in large quantities. This indicates that the removal of sulfate by hydrogen is a one-step process controlled in the dilute state only by accessibility of sulfate ions to hydrogen. The release of sulfate at temperatures less than 550°C is not complete, and the total extent of conversion of sulfate ions to hydrogen sulfide is affected by the sulfate distribution, particle surface area and porosity, and the reduction temperature.

Although activation of uranium dioxide by sulfate is now a generally accepted practice, this method fails to activate all oxides uniformly, since variations in calcining or reduction conditions sometimes produce uranium dioxide products with differing reaction characteristics. Orrick and associates[4] have developed a process by which parent uranium feed materials of widely variable reactivity and composition may be converted to a uniformly reactive uranium dioxide. The results of laboratory-scale tests have shown that uranium dioxide of

high reactivity toward hydrofluorination can be produced by a three-step activation process which involves a single air-oxidation step between an initial and a final reduction step. The suggested conditions for the production of reactive UO_2 are: reduction of the feed-material oxide by hydrogen at 675°C; oxidation of UO_2 in air at 350°C to produce U_3O_8; and reduction of U_3O_8 by hydrogen at 560°C to produce reactive UO_2. The results of this study indicated that, by utilizing this activation procedure, uranium tetrafluoride of high assay can be produced from various feed materials without the necessity of making major changes in the process conditions due to variations in the uranium dioxide reactivity.

Oxidation Behavior of Uranium Dioxide

Scott and Harrison[5] have studied the oxidation behavior of uranium dioxide powder in air at temperatures up to 800°C. Under conditions of linearly increasing temperature, uranium dioxide powders of high surface area (>1 m^2/g) were observed to oxidize in a two-step process, first to a tetragonal phase of composition $UO_{2.35}$ (U_3O_7), and then to U_3O_8. An activation energy of 19.1 kcal was derived for the $UO_2 \rightarrow U_3O_7$ oxidation step. Uranium dioxide of low surface area (<0.05 m^2/g) exhibited only a single-stage oxidation to U_3O_8.

Reduction of Uranium Trioxide by Dissociated Ammonia

Zhukovskii and Vlasov[6] have studied the effects of added alkali carbonates (Li_2CO_3, Na_2CO_3, and K_2CO_3) on the rate of reduction of uranium trioxide by decomposed ammonia. It was observed that the presence of carbonates retards the reduction, with the retarding effect increasing in the sequence Li_2CO_3-Na_2CO_3-K_2CO_3. This effect is attributed to the formation of surface layers of uranates on the uranium trioxide. In a similar study[7] it was shown that the reduction of uranium trioxide by dissociated ammonia is accelerated by the addition of 5 mole % ZnO or 5 mole % TiO_2.

Development of Other Processes for Uranium Dioxide Production

Warren and Finlayson[8] have reported studies on the reduction of uranyl carbonate slurries to uranium dioxide with formaldehyde sulfoxylates and mixtures of formaldehyde and ammonium bisulfite. Uranyl carbonate was prepared by heating aqueous suspensions of hydrated uranium trioxide for 1 hr at 130°C under a carbon dioxide partial pressure of 100 psi. Demonstration tests were performed using a high-pressure autoclave equipped with a stirrer. The reduction procedure involved placing 3 liters of slurry containing 65 g of uranyl carbonate into the autoclave, heating to operating temperature (202 to 228°C) under 100 psi carbon dioxide pressure, and, finally, injecting the reducing agent.

Although uranium dioxide of high surface area was produced by reduction of uranyl carbonate with sodium formaldehyde sulfoxylate, the oxide was found to be highly contaminated with sodium (0.5 wt.%) and did not sinter to high-density compacts. Confirmation of the deleterious effect of sodium on the sintering behavior of UO_2 powder was obtained[8] in a test employing ammonium formaldehyde sulfoxylate as the reductant. In this case the UO_2 product exhibited excellent sintering properties. However, since sodium is an undesirable impurity in UO_2, reduction with sulfoxylates would only be feasible if the ammonium salt of formaldehyde sulfoxylate was commercially available.

Preliminary experiments showed[8] that formaldehyde, in the presence of ammonium bisulfite, reduced uranyl carbonate to uranium dioxide. Formaldehyde, alone, was inactive. The role of ammonium bisulfite in the reduction appears to be that of a catalyst. The uranium dioxide produced in reductions with formaldehyde–ammonium bisulfite mixtures contained 0.05 wt.% each of carbon and sulfur, had a surface area of 3 m^2/g, and yielded compacts of high density (10.6 g/cm^3) when sintered.

Benedict and associates at Hanford Atomic Products Operation[9] (HAPO) have published a review of Hanford work on the development of a process for electrodepositing coarse crystalline uranium dioxide from a fused-chloride electrolyte. The process is based on the fact that crystalline uranium dioxide, suitable for use as a power-reactor fuel, can be prepared by the reduction of uranyl chloride dissolved in molten chloride salts. Details of the HAPO process have appeared in a previous Review.[10]

Workers at Comitato Nazionale per l'Energia Nucleare[11] in Rome have studied a process for the wet preparation of uranium dioxide powders of high surface area and capable of being sintered to high-density compacts. The process involves the reduction of a solution of uranyl

chloride with zinc to produce uranous chloride. Precipitation of uranous hydroxide is effected by the addition of ammonium hydroxide to the uranous chloride solution. Uranium dioxide powder is prepared by drying the precipitate in a hydrogen atmosphere at 600°C. Current efforts are directed toward determining the effects of precipitation and drying conditions on the final sintered density of UO_2 compacts.

In other work,[12] uranium dioxide has been synthesized directly by the high-temperature reduction of uranyl sulfate solutions with elemental sulfur vapor. It was observed in laboratory tests that the reaction proceeds with the formation of a U_3O_8 intermediate compound and that only after a period of 20 hr is pure uranium dioxide produced.

Halle[13] has described the method employed in the production of sintered uranium dioxide pellets at the Allmanna Svenska Elektriska Aktievolaget (ASEA) plant in Vasteras, Sweden. The uranium dioxide feed material for pellet fabrication is produced by homogeneous precipitation of a pure uranyl nitrate solution with urea. The powder is mixed with a lubricant, pressed, and sintered at 1700°C to a density 98% of theoretical. The pellets are ground to close diameter tolerances and then inserted in the fuel-element canning tubes.

Coating of Uranium Dioxide Particles

The encapsulation of uranium dioxide particles within a ceramic or metallic coating provides a potentially significant corrosion and radiation-damage-resistant reactor fuel material for use at conditions of high temperature and high burnup. Browning and associates[14] at Battelle Memorial Institute (BMI) have developed a process for depositing pyrolytic carbon coatings on UO_2 and UC_2 particles by chemical vapor-deposition reactions in a fluidized bed of the particles. Uranium dioxide when brought in contact with graphite at about 1200 to 1300°C normally starts to react, releasing carbon monoxide, but encapsulation of the particles in pyrolytic carbon prevents escape of carbon monoxide, and no reaction is expected to occur. The vapor deposition of pyrolytic carbon by the pyrolysis of benzene, toluene, propane, methane, and acetylene was investigated. Carbon coatings were deposited from all these hydrocarbons, but the pyrolysis of benzene, toluene, and propane tended to produce sooty by-products that eventually plugged the reactor exhaust system. The pyrolysis of acetylene proceeded more rapidly than that of methane below 1500°C, and acetylene was generally used to deposit coatings at temperatures below 1500°C, whereas methane was employed at temperatures above 1500°C.

The fluidized-bed reactor employed in tests to coat particles with pyrolytic carbon at temperatures up to 1500°C consisted of a 1-in.-ID mullite tube with a conical bed support. The fluidizing gas (helium) and hydrocarbon gas were introduced into the reactor through a $^3/_{64}$-in. hole at the center of the bed-support cone. The gas mixture was preheated to 600 to 700°C before entering the reactor. The equipment used for coating particles at temperatures above 1500°C consisted of a cone-bottom $^3/_4$-in.-ID graphite tube enclosed in a Vycor envelope and insulated with carbon black. To prevent oxidation of the carbon black and the graphite reactor tube, the annulus between the reactor and envelope was purged with helium.

A two-step deposition procedure was designed to minimize uranium contamination of the coatings. Bare fuel particles were first coated with 5 to 10 μ of pyrolytic carbon. The coated material was then leached in concentrated nitric acid for 20 min at room temperature. After the leached material was washed in alcohol and dried, pyrolytic carbon deposition was continued in a reactor which had not been exposed to bare fuel. This procedure eliminated the possibility that any UC_2 or UO_2 dust which collected in the top of the reactor might feed back into the reaction chamber and contaminate the coating.

Carbon coatings were satisfactorily deposited by pyrolysis of acetylene on both UC_2 and UO_2 substrates. Coatings with good integrity were prepared at temperatures from 950 to 1400°C. Deposition rates between 2 and 1200 μ/hr at 1400°C were obtained, with the low rate favoring the formation of columnar pyrolytic carbon and the higher rates a porous deposit of laminar pyrolytic carbon.

Satisfactory coatings were also prepared by the pyrolysis of methane at temperatures from 1500 to 1600°C on either UO_2 or UC_2 particles. Typical coated UO_2 particles are shown in Fig. V-1. The structure of the coating depended on the deposition rate. Contamination of the coating by migration of uranium during the coating process was a problem when coatings were prepared at 1600°C and above. Migration of ura-

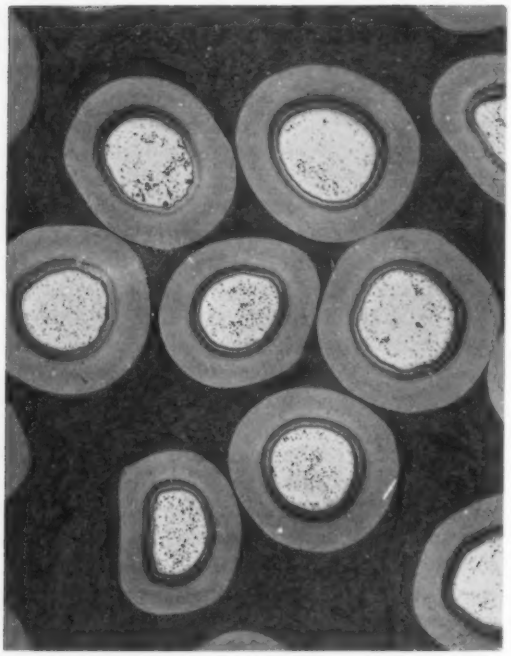

Fig. V-1 127-μ enriched UO_2 coated with 66 μ of pyrolytic carbon by pyrolysis of methane[14] at 1600°C. (Courtesy of Battelle Memorial Institute.)

nium was considerably more pronounced with UC_2 particles than with UO_2 particles.

Coating temperature had a marked effect on coating efficiency (i.e., the fraction of carbon in the feed material deposited on the particles). The coating efficiency was reduced from an average of about 55% at 1400°C to only a few percent at 950°C. Also, the average efficiency obtained with methane at the higher temperature was greater than that obtained with acetylene at 1400°C (approximately 70% for methane and 55% for acetylene). Methane, with its higher activation energy for decomposition, would be expected to pyrolyze preferentially at the particle surface to a greater extent than would acetylene. This would result in less soot formation and higher coating efficiencies.

Composite coatings (ceramic inner layer overcoated with pyrolytic carbon) and duplex coatings with pyrolytic carbon of mixed structures have been prepared. Irradiation tests with 200-μ-diameter particles coated with pyrolytic carbon 60 μ thick showed that fission-gas retention at temperatures from 20 to 1000°C was not satisfactory. However, much more satisfactory results have been shown with composite coatings consisting of metal oxides and pyrolytic carbon. Thicker (110 μ) coatings of pyrolytic carbon have also exhibited satisfactory fission-gas retention. The resistance of ceramic coatings to reactions with oxygen and graphite is the subject of a recent report.[15]

Coating of Uranium Dioxide Particles with Niobium

Workers at Société d'Études de Recherches et d'Applications pour l'Industrie (SERAI), Brussels,[16,17] are investigating a process for depositing niobium metal on individual particles of uranium dioxide. The process involves the reduction of niobium pentachloride by hydrogen in a fluidized-bed reactor. This technique is based on earlier work performed at BMI and reported in a previous Review.[18] It was observed,[16,17] in tests performed in a quartz fluid-bed apparatus, that the best metallic coatings were obtained at temperatures from 850 to 900°C.

Costs of Coating Fuel Particles

Oxley and associates[19] at BMI have published an estimate of costs for coating nuclear fuel particles. The preliminary estimates show that carbon coatings are the least expensive type being studied at present, that alumina coatings are an order of magnitude more expensive, and that beryllium oxide coatings are even more costly because of the high cost of beryllium metal feed. For commercial quantities of 40-μ coatings on 127-μ fuel particles, the more optimistic coating prices are approximately 0.02 mill/kw-hr for carbon coatings, 0.1 mill/kw-hr for alumina coatings, and 1 mill/kw-hr for beryllium oxide coatings at 10,000 Mwd/ton burnup on the basis of previous estimates for reactors having thermal efficiencies of 28%.

Preparation of Uranium Carbides and Other Ceramic Materials

Preparation of Uranium Carbides

Workers at General Telephone and Electronics Laboratories[20] have continued the study of a process for converting uranium tetrafluoride to uranium carbide. Previous work on this project was reported in the January 1963 issue of

Reactor Fuel Processing.[21] The process involves the heating of compacts prepared from a blended mixture of uranium tetrafluoride, silicon, and carbon to temperatures from 1200 to 1800°C in a vacuum. The reaction can be represented as $UF_4 + Si + C \rightarrow UC + SiF_4$. It was observed[20] that the yields of uranium carbide were increased by conducting the reaction at temperatures below 1400°C and by reducing the particle size of the reactants. The optimum conditions for producing high-purity uranium carbide were found to include heating the compacts for 24 hr at 1350°C under a furnace pressure of 500 μ. The results from five tests showed that uranium monocarbide prepared under these conditions contained residual fluoride and silicon values below 100 and 150 ppm, respectively. Oxygen and nitrogen contents were below 800 ppm, and the carbon content was found to be 5.0 ± 0.1 wt.%. Densities of the product averaged 13.9 g/cm^3. The yield of uranium carbide obtained in the laboratory-scale reactor ranged from 70 to 80%. It is expected that the yield of uranium carbide would be markedly increased through the use of a moving-bed reactor concept described in a previous Review.[21]

Among the most promising methods for preparing uranium monocarbide is the reaction between uranium dioxide and elemental carbon at high temperatures. Workers at Nuklear-Chemie und -Metallurgie G.m.b.H. (NUKEM)[22,23] have been conducting a development program to evaluate the preparation of uranium monocarbide from powdered mixtures of uranium dioxide and carbon. The study included an evaluation of uranium dioxide prepared under several different processing conditions. It was concluded that UO_2 produced from ammonium diuranate by calcination and reduction at 800°C was the most suitable feed material. Natural graphite with an ash content of 0.06 wt.% was used as the source of carbon. Intimate contact between the powdered reactants was achieved by compressing the blended feed materials into spherical pellets prior to reaction. In tests, pellets were fabricated in a rotary press, without the use of a binder, to a density of 4.5 g/cm^3. The pellets were then reacted in a graphite crucible at 1700°C under reduced pressure. Since the total time required to process a batch of pellets in the crucible was 24 hr, including heating and cooling periods, a semicontinuous crucible furnace facility is being constructed to demonstrate higher production rates. In this facility[24] the spherical pellets are fed intermittently into the crucible maintained at a temperature of 1600°C. When the entire charge has been fed, the temperature of the crucible and contents is raised to 1700°C. After the reaction is complete, the uranium monocarbide product is removed from the system through a sliding valve located at the bottom of the crucible.

Uranium monocarbide produced by the batch process[23] had a density of 9 g/cm^3. The oxygen content of the product was 0.1 wt.%, and the carbon content ranged from 4.7 to 4.8 wt.%. The uranium monocarbide product was successfully arc melted and cast into rods.

Colombo and Steinberg at Brookhaven National Laboratory (BNL)[25] have attempted to prepare uranium monocarbide by the reaction between uranium metal and propane in a gamma-radiation field. A series of survey experiments was performed to determine the effect of temperature, reactant concentration, and radiation dose on the yield of uranium monocarbide. The results indicated that gamma radiation has a small effect in promoting the uranium-hydrocarbon reaction. Raising the temperature from 26 to 350°C or the concentration of propane from one to five times the stoichiometric requirement did not significantly increase the yield of uranium monocarbide. At room temperature the maximum conversion to carbide was 5%.

Williams[26] has developed a method for preparing porous uranium dicarbide spheroids with densities from 60 to 70% of theoretical by reaction of uranium dioxide and carbon. The process involves the compaction of a mixture of uranium dioxide and carbon followed by granulation and spheroidization of the compacts on an abrasive track. Uranium dicarbide spheroids having diameters of 100 to 700 μ have been prepared by reacting the compacts at 1400°C under vacuum.

The development of advanced types of nuclear reactors has underlined the importance of uranium carbides and plutonium carbides as fuel materials. Accary[27] has published a review of the different methods of preparing and forming uranium carbides relevant to their use as fuel materials. The International Atomic Energy Agency (IAEA) has published[28] a critical evaluation of the thermodynamic data on uranium carbides and plutonium carbides. This report represents the views of a panel that was organ-

ized to assess the available thermodynamic data and to recommend those values which were considered to be most reliable.

Coating of Uranium Carbides

A principal difficulty in the design of a nuclear reactor employing uranium carbide as the fuel material is the reactivity of the fuel with moisture to form oxide. This problem is paramount in fabrication operations. Bradley and Ferris[29] have studied the hydrolysis of uranium monocarbide by liquid water in the temperature range from 25 to 100°C. It was observed that, when uranium monocarbide was allowed to react with water at temperatures between 25 and 99°C, an insoluble, gelatinous, greenish-brown tetravalent uranium compound was formed along with a gas consisting chiefly of methane (86 vol.%), hydrogen (11 vol.%), and small quantities of saturated hydrocarbons containing two to seven carbon atoms. All of the carbon originally present in the monocarbide was converted to gaseous products. Although temperature had no observable effect on the composition of the gaseous reaction products, the rate of hydrolysis increased markedly with increasing temperature. In other work, Kempter[30] investigated the hydrolysis properties of uranium monocarbide and uranium dicarbide and observed that UC_2 hydrolyzed in water much more rapidly than did UC.

Workers at BMI[14] have developed a technique for coating carbide fuel particles with carbon films to protect the carbide against attack by humid air during the fabrication operation. A description of the coating procedure is given under the heading "Coating of Uranium Dioxide Particles" in this section.

Pyrolytic carbon coatings provide excellent protection for uranium carbides against attack by moisture. A series of tests performed at Oak Ridge National Laboratory (ORNL)[31] on uranium dicarbide particles coated with laminar type pyrolytic carbon showed that this coating is protective against prolonged exposure to water vapor at temperatures below 800°C. The extent to which the particles remain protected was found to vary considerably among different lots of coated particles. At 1100°C it is unlikely that any coatings will remain intact for as long as 1 hr.

Benesovsky and Rudy[32] have described a program being conducted at Metallwerk Plansee AG. for the production of dense graphite coatings on uranium- and thorium-containing carbides. The coatings are formed by pyrolytic decomposition of hydrocarbons. A semiautomatic fluidized-bed apparatus has been designed for producing coatings at temperatures up to 2200°C. On the basis of the work at Metallwerk Plansee, a prototype fluidized-bed apparatus has been developed for preparing coated particles for the Dragon Reactor Experiment.[33] A diagram of the fluid-bed reactor, which has recently been commissioned, is shown in Fig. V-2. The reactor, having a capacity of 760 cm^3, is constructed of graphite with an internal diameter of 2 in. The unit is equipped with a water-cooled nozzle system. The center nozzle, which is constructed of molybdenum, conveys the hydrocarbon-containing gas into the reactor. The inert carrier gas enters through an annular space surrounding the center nozzle. Incorporation of this nozzle design makes possible the prevention of carbon deposition at the entry zone of the reactor. The particle-charging apparatus and the gas-exhaust system are located at the top of the fluid-bed reactor. Particles are fed through a molybdenum tube into the reactor. The exhaust gases are passed through a filter system consisting of eight exchangeable filter units packed with silica fiber.

Plutonium-Containing Carbides

Interest in fast reactors has revealed a need for a breeder type fuel consisting of some form of plutonium associated with natural uranium. Of considerable interest for this type of application is a solid solution of plutonium monocarbide in uranium monocarbide. Strasser, Taylor, and Anderson[34] have investigated the preparation of a 20 mole % plutonium monocarbide–80 mole % uranium monocarbide solid solution. The procedure involved the carbon reduction of a 4 to 1 mixture of uranium dioxide and plutonium dioxide. The oxide-carbon mixture was blended and then pressed at 5000 psi, without binder, into right cylinders. The solid solution of uranium monocarbide–plutonium monocarbide was prepared by reacting the compacts in a graphite crucible at 1550°C for 5 hr followed by 1 hr at 1625°C. It was observed that, to avoid the formation of plutonium sesquicarbide (Pu_2C_3) in the product, approximately 95% of the stoichiometric amount of carbon should be added to the feed material. Higher carbon concentrations produce the undesirable sesquicarbide phase.

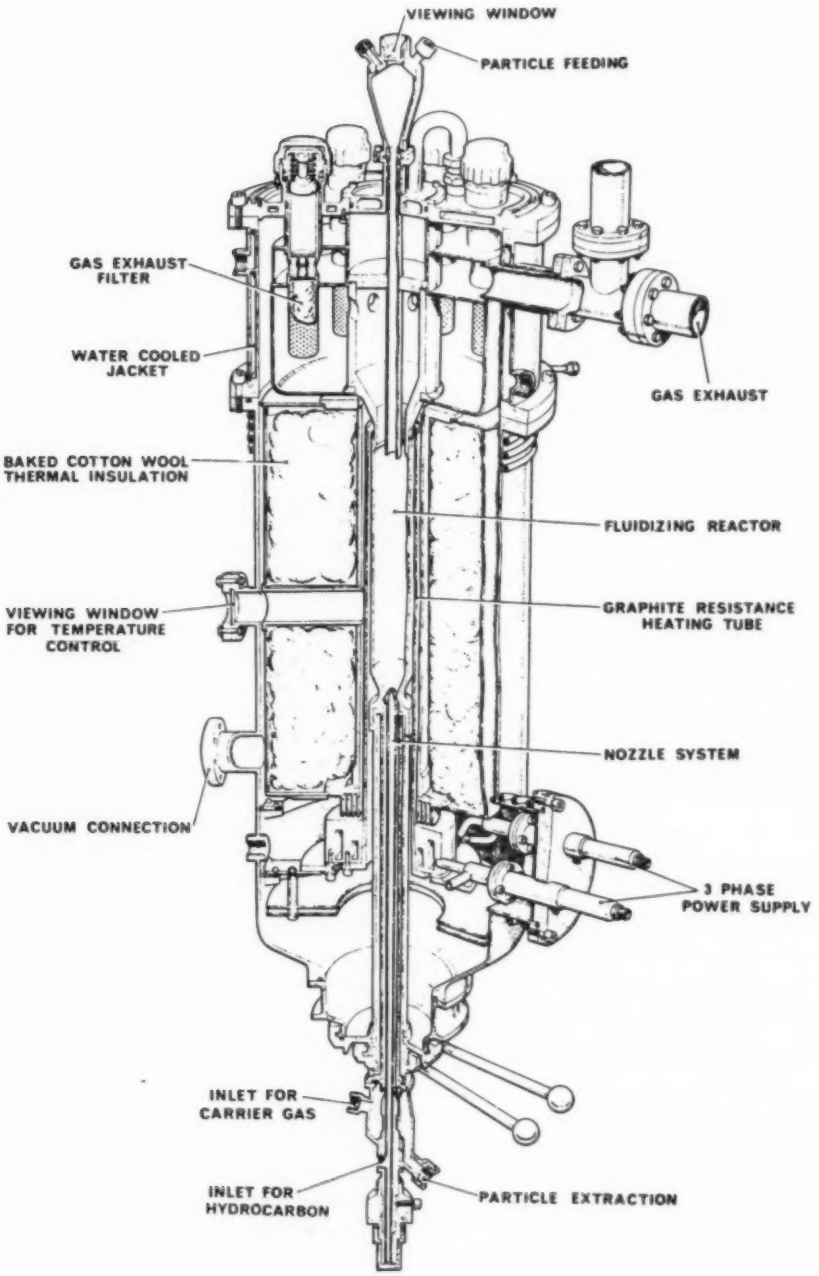

Fig. V-2 Prototype production-scale fluidized bed for the coating of carbide particles.[33]

It has been observed[34] that free carbon hinders densification of uranium monocarbide–plutonium monocarbide during sintering. It was also observed that the addition of 0.12 wt.% nickel powder to the compacts increases markedly the final density of sintered compacts.[34,35] The effect of nickel addition on sintered density is less pronounced in pellets containing as little as 0.10 wt.% free carbon. In a series of tests involving the fabrication of $(U_{0.95}Pu_{0.05})C_{0.98}$ pellets, it was observed[35] that pellets containing 0.12 wt.% nickel sintered to high density (13 g/cm^3) in 0.5 hr at 1550°C, whereas pellets without nickel required 1 hr at 1925°C to achieve equivalent densities.

The uranium-plutonium-carbon ternary phase diagram for the composition range from 0 to 50 at.% carbon and for temperatures below 635°C has been reported by Rosen, Nevitt, and Barker of Argonne National Laboratory.[36] In connection with this work, the uranium monocarbide–plutonium monocarbide system was studied in some detail.[37] Uranium monocarbide forms a complete series of solid solutions with plutonium monocarbide. The (U,Pu)C phase is stoichiometric with regard to its carbon content in a composition range from 0 to 35 at.% plutonium. With further increase in plutonium content, the phase deviates from ideal stoichiometry toward metal-to-carbon ratios greater than 1 to form a defect (U,Pu)C phase.

Thorium-Uranium Carbides

The fuel and fertile material for the Peach Bottom High-Temperature Gas-Cooled Reactor (HTGR) are in the form of carbides uniformly dispersed as particles in a portion of the graphite moderator. A process that has been developed for the preparation of $(Th,U)C_2$ particles by the carbon reduction of the oxides has been described by Goeddel.[38] Agglomerated particles of thorium oxide, uranium dioxide, and carbon are prepared by mixing powdered ThO_2, UO_2, carbon, and ethyl cellulose in trichloroethylene to form a slurry. The particles are dried at 60°C and sieved to obtain a size fraction between 495 and 295 μ in diameter. The particles are then dispersed in graphite powder, loaded into a graphite crucible, and heated to a temperature from 2100 to 2300°C. Under these conditions the oxides are converted to the dicarbides. After the reaction is complete, the temperature of the charge is raised above the melting point of the carbides (2450°C) to densify the particles. The powdered graphite bed prevents the dicarbide particles from flowing or sintering together. Particles prepared by this procedure were found to be of high density, and the results of X-ray analyses showed the material to be $(Th,U)C_2$.

Thorium-uranium dicarbide is extremely reactive with moisture, and fuel compacts containing unprotected $(Th,U)C_2$ disintegrate by hydrolysis after a few hours' exposure to air. A process for coating $(Th,U)C_2$ particles with carbon films to protect the carbide against attack by water vapor has been developed at General Atomic.[38,39] This process is based on work performed at BMI.[14] The coating is accomplished in a fluidized-bed apparatus using a methane-helium mixture at a temperature of 1400°C.

Uranium Nitride and Uranium Beryllide

Workers at BMI[40] have been investigating the fabrication and properties of uranium mononitride in an effort to determine its suitability as a power-reactor fuel. Uranium mononitride may be prepared by heating uranium metal chips in pure nitrogen for 15 hr at 850°C to form U_2N_3 and then decomposing the U_2N_3 in a vacuum at 1300°C. Dense uranium mononitride bodies cannot be obtained by vacuum sintering. It appears that during vacuum sintering at 1800°C uranium mononitride dissociates into nitrogen and uranium metal. High-density (95% of theoretical) bodies have been prepared by hot pressing for 3 hr at temperatures of 1480 to 1540°C under a pressure of 10,000 psi.

Dell and Allbutt[41] have published a complete review of the chemical and physical properties of uranium nitrides and sulfides; descriptions of the methods of preparation are included. The enthalpy of decomposition of uranium mononitride has been determined by Cavett and Bonham[42] to be 68.7 kcal/mole with a standard deviation of 2.2 kcal/mole. In other work[43] the heat of formation of uranium mononitride was determined to be -69.6 ± 0.4 kcal/mole by measuring the heat evolved in the reaction between an excess of uranium powder and a known quantity of nitrogen.

Hanna and Turner[44] have investigated methods for the preparation of uranium beryllides. The most suitable method for preparing beryllide compounds from the metal powders was reaction pressing, wherein mixtures of the constituent metal powders are simultaneously reacted

and consolidated under pressure. Good compacts of UBe_{13} were prepared by reaction pressing at 1550°C at 1 tsi. The quality of the product from preliminary tests was quite variable, and difficulty was experienced in achieving products of stoichiometric composition. The major difficulty associated with the preparation of UBe_{13} was the swelling accompanying the reaction, especially in the case where the reaction was carried out in the absence of pressure.

Production of Uranium Metal

In a review of the chemical processing of uranium concentrates, Galkin, Maiorov, and Veryatin[45] have described the methods employed in the commercial production of uranium metal. A significant feature of this text, which was originally published in the USSR in 1960, is the thorough referencing to the foreign literature on uranium processing technology.

Applications for enriched uranium have grown to the extent that processing of this material promises to become an important segment of the atomic industry. A considerable amount of report literature on the processing of enriched uranium has been published, but the entire subject was not treated in depth in one study. To fill this gap in the technical literature, Patton, Googin, and Griffith have prepared a monograph[46] on enriched-uranium processing. Of particular interest in this text are the sections devoted to radiation safety, uranium accountability and control, and plant and equipment design.

Bomb Reduction of Uranium Tetrafluoride

Uranium metal is produced at the National Lead Co. of Ohio (NLCO) by the bomb reduction of uranium tetrafluoride with magnesium in steel vessels lined with packed magnesium fluoride slag. The reduction is accomplished by heating the sealed vessel in a resistance-heated furnace maintained at about 715°C. Firing time, i.e., the heating interval required to cause initiation of the reduction, varies with the furnace temperature and with the type of uranium tetrafluoride feed material. A typical firing time at a furnace temperature of 715°C is 190 min. When the same charge is heated to 737°C, the firing time is reduced to 165 min. However, the quality of slag-metal separation is somewhat lower at the shorter firing time. If the firing time could be shortened without diminishing the yield or the quality of slag-metal separation, the capacity of the reduction facilities would be markedly increased.

Previous work at NLCO, reported in *Reactor Fuel Processing*,[47] showed that the use of lithium pellets to initiate the reaction resulted in a 20 to 30% reduction in preheat time for small-scale equipment. In present work[48] the use of lithium alloy to shorten bomb-reduction firing time was evaluated in plant-scale equipment. A series of tests was made using 50-g lithium pellets to initiate the reduction. Tests were performed at furnace temperatures of 650, 732, and 760°C. Control reductions without a lithium pellet were made at each of the three temperatures employed. Best results were obtained at a 732°C furnace temperature and with the lithium pellet placed at the inner wall of the liner at the horizontal midplane of the charge. Under these conditions the average firing time was reduced from 250 min for the control charges to 135 min for the lithium charges. The yield and quality of the slag-metal separation were comparable with those of the control reductions. Reductions made with the lithium pellet at other locations were less satisfactory. In all reductions the amount of lithium in the uranium derby (the uranium-metal product) was below the detectable limit of 1 ppm. The lithium used in this work was 98 at.% Li^7 and 2 at.% Li^6 with a cross section of 18.9 barns. On the basis of the lithium analysis of the uranium derby, the lithium remaining in the metal was equivalent to less than 0.04 ppm boron.

Production of Thorium Dioxide Particles

Spheroidal thoria and thoria-urania particles of about 1 μ average diameter have been prepared at ORNL[49] in a one-step process by flame denitration of thorium nitrate solutions and thorium nitrate–uranyl nitrate solutions. The process involves atomization of the nitrate solutions directly into a high-temperature reflected flame produced by oxygen–propane gas mixtures. Methanol was the most commonly used solvent for the thorium nitrate or thorium-uranium nitrate feed solutions, although water was satisfactorily employed in several tests. The combustion exhaust gases and the spherical

oxide particles were directed to a cooling chamber where the product was collected and the gases cooled to near-ambient temperature. A trap was placed in the line between the combustion chamber and cooler to collect oversize particles and agglomerated spheres.

Feed solutions with thorium concentrations up to 2*M* were successfully processed in the flame denitrator. The yield of 1- to 3-μ-diameter particles, however, was only 30%, which is probably not adequate for a large-scale production operation. The remainder of the oxide was collected as oversize particles in the trap. Aluminum nitrate (equivalent to 0.5 to 10 wt.% aluminum oxide in the oxide product) was added to the feed solution in order to obtain spherical oxide particles. It was observed that the maximum temperature obtained in the flame was not sufficiently high to produce a glazed, spherical thoria product. Particles produced in the absence of alumina were nonspherical and fragmented readily.

Dense particles of thorium dioxide, suitable for vibratory compaction into tubes with a bulk density approaching 90% of theoretical, have been prepared at ORNL by a sol-gel process. The steps in the sol-gel process include steam denitration of a thorium nitrate solution to form dispersible thoria; dispersion of the thoria in dilute nitric acid to produce stable sol; evaporation of the sol to form a gel; and calcination of the gel to produce thorium dioxide particles of high density. A description of the process appeared in a previous Review,[50] and details of recent development work are presented in several reports.[51–53] An application of the sol-gel process to the preparation of U^{233}-thorium oxide is described in Sec. II of this issue.

Preparation of Thorium Dicarbide by the Sol-Gel Process

A recent application of the sol-gel process has been in the preparation of thorium dicarbide particles.[52,53] Carbon with a mean particle size of 90 A is dispersed in an aqueous sol of thorium dioxide. The ThO_2-C sol is formed into spheres by dispersion into carbon tetrachloride. The spheres are set to a gel by adding isopropyl alcohol to the mixture to extract the water. As soon as the spheres are sufficiently firm to support their own weight, they are separated from the liquid and dried in air. The spheres are then fired in vacuum for 1¼ hr at 1750°C to produce thorium dicarbide. Under this firing condition, 98% conversion to thorium dicarbide was achieved. Kinetic studies have shown the carburization reaction to be first order, with an activation energy of 140 kcal/mole of thorium dioxide. Uranium-thorium dicarbide spheres have been produced in a similar manner by adding uranyl nitrate solution during the sol preparation step. (J. J. Barghusen)

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